Simulations of the Stratospheric Circulation and Ozone during the Recent Past (1980-2004) with the MRI Chemistry-Climate Model

Kiyotaka Shibata and Makoto Deushi
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Foreword

The Center for Global Environmental Research (CGER) at the National Institute for Environmental Studies (NIES) was established in October 1990. CGER’s main objectives are to contribute to the scientific understanding of global change and to identify solutions for pressing environmental problems. CGER conducts environmental research from interdisciplinary, multi-agency, and international perspectives, provides an intellectual infrastructure for research activities in the form of databases and a supercomputer system, and makes the data from its long-term monitoring of the global environment available to the public.

CGER installed its first supercomputer system (NEC SX-3, Model 14) in March 1992. That system was subsequently upgraded to an NEC Model SX-4/32 in 1997, and an NEC Model SX-6 in 2002. In March 2007, we replaced that system with an NEC Model SX-8R/128M16 in order to provide an increased capacity for speed and storage. We expect our research to benefit directly from this upgrade.

The supercomputer system is available for use by researchers from NIES and other research organizations and universities in Japan. The Supercomputer Steering Committee evaluates proposals of research requiring the use of the system. The committee consists of leading Japanese scientists in climate modeling, atmospheric chemistry, ocean environment, computer science, and other areas of concern in global environmental research. In the 2007 fiscal year (April 2007 to March 2008), sixteen proposals were approved.

To promote the dissemination of the results, we publish both an Annual Report and occasional Monograph Reports. Annual Reports give the results for all research projects that have used the supercomputer system in a given year, while Monograph Reports present the integrated results of a particular research program.

This Monograph Report describes the reproduction of historical ozone trends with a chemistry-climate model (CCM). The authors utilized the SX-6 to carry out ensemble experiments which gave a realistic reproduction of historical trends in temperature and ozone levels. It is hoped that this research will lead to the ability to predict future ozone trends using CCMs and contribute to our efforts to solve the problem of ozone depletion.

In the years to come, we will continue to support environmental research with our supercomputer resources and disseminate practical information on our results.

June 2008

Yasuhiro Sasano
Director
Center for Global Environmental Research
National Institute for Environmental Studies
Preface

This volume of CGER’S SUPERCOMPUTER MONOGRAPH REPORT series is the thirteenth publication of research results obtained by users of the supercomputer facilities at the Center for Global Environmental Research (CGER) of the National Institute for Environmental Studies (NIES). NIES assigned sufficient computer resources to the stratospheric ozone research team at the Meteorological Research Institute (MRI) to carry out numerical simulations with a chemistry-climate model (CCM). As a result, two independent Japanese CCM simulations, NIES-CCM and MRI-CCM, contributed to the Global Ozone Research and Monitoring Project Report “Scientific Assessment of Ozone Depletion: 2006” published by the World Meteorological Organization (WMO)/United Nations Environment Programme (UNEP).

Ozone depletion due to anthropogenic chlorofluorocarbons (CFCs) is a worldwide environmental problem. In the more than ten years since the Montreal Protocol on Substances that Deplete the Ozone Layer was adopted, the CFC trend, which had been increasing, has nearly leveled off or even begun to decrease. The international “Chemistry-Climate Model Validation (CCMVal)” project was established as part of the “Stratospheric Processes And their Role in Climate” (SPARC) project to use CCMs to investigate the relationship between ozone and climate for the WMO/UNEP Global Ozone Research and Monitoring Project Report. CCMVal has two major tasks: reproduction of past ozone and prediction of future ozone. This monograph reports past ozone simulation results obtained with MRI-CCM. It is my hope that this report will contribute to further progress in global environmental research, particularly with regard to stratospheric ozone depletion.

June 2008

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Head of the First Laboratory
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Simulations of the Stratospheric Circulation and Ozone during the Recent Past (1980-2004) with the MRI Chemistry-Climate Model

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Abstract

A middle-atmosphere ensemble simulation of the recent past 25 years from 1980 to 2004 has been carried out with the chemistry-climate model (CCM) of the Meteorological Research Institute (MRI), using observed forcings of sea-surface temperature, greenhouse gases, halogens, halons, volcanic aerosols, and solar irradiance variations. Five members with slightly different initial conditions are integrated in the ensemble simulation. The MRI-CCM dynamics module is a global spectral model truncated tri-angularly at a maximum wavenumber of 42 with 68 levels extending from the surface to 0.01 hPa (about 80 km) and a vertical spacing of 500m from 100 to 10 hPa. The chemistry module incorporates 51 species and 124 reactions including heterogeneous reactions. Transport of chemical species is based on a hybrid semi-Lagrangian scheme, consisting of a flux form in the vertical direction and an ordinary semi-Lagrangian form in the horizontal direction. All five members reproduced the quasi-biennial oscillation (QBO), with a period of about 27 months for wind and ozone in the equatorial stratosphere, although the phases of the QBOs are different among five members. Multiple linear regression analysis with time lags for volcanic aerosols was performed on the zonal-mean quantities of the simulated result to separate the trend, the QBO, the El Chichón and Mount Pinatubo, the 11-year solar cycle, and the El Niño/Southern Oscillation (ENSO) signals. The MRI-CCM could more or less realistically reproduce observed annual mean temperature and ozone trends, as well as the monthly trend in total ozone. The MRI-CCM also reproduced vertical multi-cell structures in tropical temperature, zonal wind, and ozone associated with the QBO, and the mid-latitude total ozone QBO in each winter hemisphere. The solar signals of annual mean temperature and ozone were well reproduced, as manifested by a maximum positive cell in the tropical upper stratosphere and a second maximum in the tropical lower stratosphere. The ENSO signals of annual mean temperature, zonal wind, and ozone were generally reproduced in the troposphere and in the lower and middle stratosphere. The increased temperature and decreased ozone volcanic signals of both El Chichón and Mount Pinatubo eruptions were overestimated.
1. Introduction

Stratospheric ozone has decreased since the late 1970s because of the increase in the levels of reactive chlorine produced by photodissociation of man-made chlorofluorocarbons (CFCs) and halons under strong ultraviolet (UV) radiation in the stratosphere. When the stratospheric temperature is very low and less than certain critical values (about 187 K and 195 K) during winter to spring, polar stratospheric clouds (PSCs) form, and on the surfaces of the PSCs heterogeneous reactions proceed, leading to the alteration of normal gas-phase partitioning of odd nitrogen (NO$_x$), odd chlorine (ClO$_x$), and odd bromine (BrO$_x$) species. Heterogeneous reactions, for example, convert reservoir species such as HCl and ClONO$_2$ into active species such as Cl$_2$ and hence enable catalytic cycles involving reactive nitrogen, chlorine, and bromine (that is, NO$_x$, ClO$_x$, and BrO$_x$) to efficiently destroy ozone. The most prominent phenomenon associated with the combined effect of the increasing halogen and PSC formation is the Antarctic ozone hole (Chubachi, 1984; Farman et al., 1985), defined as an area of total ozone of less than 220 Dobson Units (DU). The ozone hole developed almost every year from the early 1980s to the middle 1990s. Since then, its size has nearly stabilized at very severe levels with only small interannual variations, except for a few years, when planetary waves propagating from the troposphere were unusually active. Severe ozone holes are expected to continue to appear until about 2020 (Newman et al., 2006), even though the equivalent effective stratospheric chlorine (EESC) value has been decreasing since peaking in about 1998 (e.g., Randel and Wu, 2007), unless the dynamic perturbation (wave activity) is unusually strong (e.g., Newman et al., 2004). This predicted timing is because the rate of decrease of equivalent effective Antarctic stratospheric chlorine (EEASC) is expected to be very small until about 2020, after which EEASC is predicted to diminish more quickly (Newman et al., 2006). Similarly, severe ozone depletion occurs in the northern polar region whenever the winter stratospheric temperature is cold enough for PSC formation, though not as frequently as in the Southern Hemisphere (e.g., Rex et al., 2006).

Increase in the concentrations of well-mixed greenhouse gases (GHGs) such as CO$_2$, CH$_4$, and N$_2$O as a result of human activities increases the net downward terrestrial radiation at the tropopause. This radiative perturbation warms the troposphere and the continents and oceans as global warming, and simultaneously cools the stratosphere. Both stratospheric cooling and tropospheric warming can crucially affect the stratospheric circulation, because changes in tropospheric circulation affect the generation of planetary and gravity waves; this changes the divergence of waves propagating from below and, in turn, the mean meridional circulation (e.g., Sigmond et al., 2004; Butchart et al., 2006) in the stratosphere through downward control (Haynes et al., 1991). Ozone, a non-well-mixed GHG, also contributes to global warming by trapping terrestrial radiation if ozone increases in the troposphere (Lacis et al., 1990). In contrast, a stratospheric ozone increase locally warms the stratosphere and simultaneously suppresses global warming in the troposphere by blocking solar radiation. Conversely, a stratospheric ozone decrease induces cooling in the stratosphere, as demonstrated in both polar regions (e.g., Randel and Wu, 1999). Change in H$_2$O in the lower stratospheric also affects the local radiative balance and is a possible contributor to stratospheric cooling (e.g., Forster and Shine, 1997). As a result, the variations in the concentrations of well-mixed and non-well-mixed GHGs force stratospheric change directly via radiation or indirectly via dynamics driven by waves propagating from the troposphere.
Solar irradiance variations affect the stratosphere as well as the troposphere. The 11-year solar cycle is the most prominent cycle giving rise to large impacts on the stratospheric temperature (e.g., Scaife et al., 2000) and ozone (e.g., McCormack and Hood, 1996) through substantial irradiance variations of several percent at UV wavelengths. Though the total solar irradiance variation of the 11-year solar cycle is at most 0.1% (e.g., Lean et al., 1997), its signal can be detected from the upper stratosphere down to the surface in the observed geopotential data (e.g., Coughlin and Tung, 2004). Although the 11-year solar-cycle effect on the upper stratosphere is readily understood as a direct result of UV irradiance changes (e.g., Brasseur, 1993), but the mechanism of the effect on the middle and lower stratosphere has not been as well clarified. For example, Kodera and Kuroda (2002) demonstrated that the Brewer-Dobson circulation is weakened during the solar maximum via the wave-mean flow interaction in the subtropical upper stratosphere of the winter hemisphere, which induces warming and an ozone increase in the tropical lower stratosphere. However, this mechanism cannot explain the observed minimum signals of temperature and ozone in the tropical middle stratosphere.

Huge volcanic eruptions eject large amounts of SO$_2$ gas into the stratosphere, which eventually condenses into volcanic sulfate aerosols through gas-to-particle conversion. Volcanic aerosols produce large perturbations in the heterogeneous reactions on the aerosol surface as well as in radiative heating, and thereby heavily disturb stratospheric chemistry and dynamics. Giant volcanic eruptions are sporadic, but they occasionally occur, at least a few times each century (e.g., Siebert and Simkin, 2002), and the volcanic aerosols from one eruption remain in the stratosphere for up to several years, depending on the magnitude of the eruption (Deshler et al., 2006), inducing crucial variations in ozone and temperature levels in the stratosphere. For example, after the June 1991 Mount Pinatubo eruption—the largest eruption in the 20th century—record low values (two standard deviations below the normal value, i.e., -2$\sigma$) of global (65°S to 65°N) total ozone (e.g., Gleason et al., 1993) and anomalously warm (+3$\sigma$) zonal mean temperature in the middle stratosphere (e.g., Labitzke and McCormick, 1992) were observed.

Numerical simulations, in particular with general circulation models (GCMs), are required to investigate the role of each forcing on dynamics variations in the stratosphere, because the dynamics and physical processes of the atmosphere are fully non-linear. There are two ways to perform GCM simulations, by the time-slice (or equilibrium) method or by the time-varying (or transient) method. When the time-slice method is employed, the response is assumed to be the difference between the control run and an experimental run, in which target forcings over a certain period are added and held constant. Langematz et al. (2003), for example, simulated the changes in the stratosphere since 1979 by imposing an O$_3$ decrease and a CO$_2$ increase. On the other hand, with the time-varying method, realistically evolving target forcings are imposed. For example, Ramaswamy et al. (2006) evaluated each effect of different forcings on observed two pronounced step-like transitions observed in global lower stratospheric cooling during 1979-2003.

Chemical transport models (CTMs) and chemistry-climate models (CCMs) are very useful for investigating changes in the levels of stratospheric ozone or other constituents, despite their having different frameworks, because ozone and other constituents are prognostic variables in these models. CTMs are forced by observed or GCM-generated
meteorological fields without feedback between chemistry and dynamics via radiation, whereas CCMs use GCM-generated meteorological fields with feedback. To date, time-slice and time-varying simulations focusing on stratospheric ozone have been carried out with both CTMs focusing on the stratospheric ozone (e.g., Chipperfield, 1999; Hadjinicolaou et al., 2005; Stolarski et al., 2006) and with CCMs (e.g., Austin et al., 2003; Dameris et al, 2005; Tian and Chipperfield, 2005; Austin and Wilson, 2006; Garcia et al., 2007). CCMs of the stratosphere cover a wide range of integration periods and exhibit different complexities in their chemistry and dynamics modules. For example, Austin et al. (2003) evaluated uncertainties in, and assesses, seven CCMs and one GCM using parameterized chemistry, with a particular focus on polar ozone. Following this, Eyring et al. (2006) similarly compared simulations among thirteen CCMs simulations, including that of the Meteorological Research Institute (MRI), over two or more recent past decades using the specification of the reference simulation 1 (REF1) common scenario of the Chemistry-Climate Model Validation Activity (CCMVal) for the Stratospheric Processes And their Role in Climate (SPARC) project (Eyring et al., 2005). The REF1 scenario includes nearly all of the forcings for which observations are available, such as sea-surface temperature (SST), sea ice, well-mixed GHGs, halogens, halons, the 11-year solar cycle, and volcanic aerosols.

This study describes long-term variations and trends in the REF1 simulation for 1980-2004 by the CCM of the MRI (MRI-CCM), focusing on different aspects than the analysis of Eyring et al. (2006). The simulation data used in this study are based on a new REF1 simulation. This data set differs from that used by Eyring et al. (2006) in their CCM intercomparison, because the transport scheme for chemical constituents was thoroughly updated to decrease model biases in chemistry after the data had been submitted for the intercomparison. Multiple linear regression analysis was applied to temperature, zonal wind, and ozone to objectively separate the trend, quasi-biennial oscillation (QBO), El Chichón and Mount Pinatubo, 11-year solar cycle, and El Niño/Southern Oscillation (ENSO) signals, and the simulation results and observation data were compared for each signal.
2. Model Description

2.1 Dynamics Module

2.1.1 Dynamics

MJ98 GCM (Shibata et al., 1999) is used as the dynamics module, and it includes major physical processes in the troposphere and middle atmosphere. MJ98 is a full, primitive equation model that uses a spectral transform method in which spectral waves are triangularly truncated at a certain maximum wavenumber. The standard version uses triangular truncation and a maximum total wavenumber 42 (T42), the corresponding resolution of which is the associated Gaussian grids of 128 × 64 in longitude and latitude spaced about 2.8° (~300 km). In the vertical direction, a finite difference method is used with a lid at 0.01 hPa (about 80km). The current version possesses 68 levels (L68), which have a vertical spacing of about 500 m from 100 to 10 hPa with tapering below and above in order to simulate the QBO (Shibata and Deushi, 2005a), whereas the standard version has 45 levels (L45) (Shibata et al., 2005), with a vertical spacing of about 2 km in the stratosphere (Fig. 1).

The vertical coordinate is a sigma-pressure hybrid coordinate (Simmons and Burridge, 1981), which is terrain-following in the troposphere and becomes a pressure coordinate above about 50 hPa in the middle atmosphere. In L68 vertical thickness was made to coincide with that of L45 below about 150 hPa to minimize the impact of the middle atmosphere vertical thickness on the tropospheric climate. Time integration is performed by the semi-implicit method (Hoskins and Simmons, 1975) and uses a weak time filter (Asselin, 1972). The time step is determined automatically by the model to satisfy the Courant-Friedrich-Lewy (CFL) condition.

Biharmonic ($\nabla^4$) horizontal diffusion is weakened in the middle atmosphere from that in the troposphere to reproduce the QBO (Shibata and Deushi, 2005a). The e-folding time at the maximum total wavenumber of 42 is 18 hours (coefficient: $0.78 \times 10^{16} m^4 s^{-1}$) below 150 hPa, and 100 hours ($0.14 \times 10^{16} m^4 s^{-1}$) above 100 hPa, and interpolated values in between, leading to a period of about 27 months for the QBO, as will be described later. Note that this e-folding time above 100 hPa differs from that (180 hours) used in Shibata and Deushi (2005a), wherein the QBO period is about 31 months.

The e-folding time of the horizontal diffusion should be long enough to minimize its effect on the QBO temporal and spatial structure. For a Gaussian meridional structure centered at the equator with a $15^\circ$ e-folding latitude, almost all of the power (> 99%) is represented by the first several waves (Legendre polynomials) with a total wavenumber of less than 10 ($n < 10$) (Shibata and Deushi, 2005a). The e-folding time of the weakened horizontal diffusion, 100 hours at total wavenumber 42 ($n = 42$), resulted in an e-folding time of about 3.5 years at $n = 10$, a time scale that is much larger than the QBO period.

2.1.2 Convection

The Arakawa-Schubert (1974) scheme is used for deep convection with a prognostic closure similar to that of Randall and Pan (1993). The vertical profile of upward mass flux is simplified to be a linear function of altitude, following the method of Moorth and Suarez (1992). The thermodynamic properties of the upward mass flux at the cloud base, which is fixed at a level near 950 hPa, are determined by the vertical mean of the grid-scale values below the cloud base. The effect of wind shear responsible for the
vertical tilting of cumulus clouds is taken into account, as is convective downdraft. Mid-level convection is also included in the model. Clouds form at the level of the highest moist static energy in the vertical column and the mass flux is determined under the condition that large-scale moisture increases are spent by convection.

2.1.3 Radiation

A multi-parameter random model is used for terrestrial radiation. There are four spectral intervals—20-550, 550-800, 800-1200 and 1200-2200 cm$^{-1}$—and five gases. H$_2$O is considered to show continuum absorption in all intervals, whereas CO$_2$ (15 $\mu$m) is included in the second spectral intervals, and O$_3$ (9.6 $\mu$m) is included in the third spectral intervals (Shibata and Aoki, 1989). In addition to these three gases, N$_2$O (7.8 $\mu$m) and CH$_4$ (7.6 $\mu$m) are incorporated in the fourth spectral interval (Shibata et al., 1999). Full- and half-level temperatures are calculated from the prognostic layer-mean temperature profile (Shibata and Uchiyama, 1994), and a two-grid noise-suppressing scheme is included in the integration of the transmission function (Shibata, 1989). Cloud is treated as a gray body, and its optical depth is set to be proportional to the cloud water path with the use of effective emissivity (Stephens, 1978).

Delta-two-stream approximation is used for solar radiation. Spectral intervals, the k-distribution data and the absorption cross section are taken from the work of Briegleb (1992); O$_3$ in the ultraviolet (seven intervals in the 0.2-0.35 $\mu$m band) and visible (one interval in the 0.35-0.7 $\mu$m band) regions, H$_2$O in the near-infrared region (7-k interval in the 0.5-5.0 $\mu$m band), CO$_2$ (2.7 and 4.3 $\mu$m), and O$_2$ (A and B bands) are considered. Optical properties of clouds in each band are based on the work of Slingo (1989). Delta-two-stream calculation for transmission and reflection is implemented by the discrete ordinate method (Shibata and Uchiyama, 1992).

Solar declination is calculated from the orbital parameters at a specified epoch, namely, eccentricity, obliquity, longitude of perihelion, mean motion, and mean anomaly, which give the Sun-Earth distance and the true anomaly as functions of date. In addition, the difference between the apparent and mean solar times is considered.

Cloud fraction is diagnosed from a quadratic function of relative humidity in each layers, and clouds are not formed below critical relative humidity values, which depend on pressure level. Cloud overlap is calculated by using a specified correlation such that the overlap approaches a maximum between near-level clouds but is random between far-level clouds.

2.1.4 Vertical Diffusion and Ground Hydrology

The level 2 turbulence closure scheme of Mellor and Yamada (1974) is used with the mixing length of Blackadar (1962), in which the asymptotic mixing length is set at 300 m. Surface flux is represented by the bulk method and the drag coefficients are based on those of Louis et al. (1982). The roughness parameters over land are determined from the vegetation type in the simple biosphere scheme (SiB) (Sellers et al., 1986), whereas the roughness parameter over the ocean is taken from the work of Charnock (1955).

The ground hydrology scheme, which is based on the force restore method (Deardorff, 1978), is so improved from that of the original SiB; in the improved scheme, three soil layers are used for both heat and moisture. Thus, temperature and moisture are defined
2. Model Description

in the same layers, so heat and water budgets are consistent with each other. As a result, the phase transition of water—melting and freezing—can be rigorously treated.

2.1.5 Gravity Wave Drag

The orographic gravity wave drag (GWD) developed by Iwasaki et al. (1989) is used, in which gravity waves are partitioned according to horizontal wavelength into long (wavelength > 100 km) and short (wavelength ~ 10 km) waves. The long waves propagate upward, penetrating the troposphere and depositing momentum in the middle atmosphere, whereas the short waves are trapped in the troposphere and exert drag therein. The momentum fluxes of both long and short waves are excited by orographic variance of sub-grid scale, but the form (and hence magnitude) of the orographic variance and the way momentum is deposited are different.

Instead of Rayleigh friction, which is employed in the standard version (Shibata et al., 2005), the non-orographic GWD scheme by Hines (1997) is introduced, and its source strength (root mean square [RMS] wind perturbation) is enhanced symmetrically with respect to the equator between 30°S and 30°N by superimposing a Gaussian function source (0.7 m s⁻¹) on an isotropic source (2.3 m s⁻¹) (Fig.2), resulting in a maximum RMS wind of 3.0 m s⁻¹ over the equator. The gravity wave source in the tropics is similarly enhanced in the QBO simulation of the UK Unified Model (Scaife et al., 2000). The gravity wave spectrum is isotropically launched to eight equally spaced azimuths (north, northwest, west, etc) at the lowest level with a horizontal wavenumber $k^* = 5.0 \times 10^{-6}$ (m⁻¹). In addition, vertical diffusion is switched off in the stratosphere to keep the sharp vertical shear in the QBO.

2.1.6 Relaxation to Observed Field

A forcing term that relaxes to the observed field (that is, a nudging term) can be added as an option to MJ98-CCM to diminish the systematic bias of the dynamics module. The nudging term with respect to wind, for example, is expressed by

$$- \frac{u - u_{obs}}{\tau},$$

where $u$ is the simulated winds and $u_{obs}$ is the observed winds, and $\tau$ is the e-folding time, which was set to 24 hours after some sensitivity tests. Nudging is crucial for reproducing atmospheric fields during specific events, periods, or years because the simulated field tends to deviate from the initial observed field and begins to approach to the model climate within about two weeks. Nudging is applied to zonal and meridional winds but it is not used for temperature because nudging of temperature produces additional diabatic heating and directly induces artifactual meridional circulation, which in turn has undesired effects on the distribution of chemical species.

2.2 Chemistry Module

The chemistry module consists of two processes: transport and chemistry. The chemistry process is composed of the following sub-processes: photodissociation, chemical reaction (gas phase and heterogeneous), PSC formation, time integration, PSC sedimentation, deposition (dry and wet), and vertical diffusion.
2.2.1 Transport

The transport scheme for chemical species is, unlike that used in the dynamics module, a hybrid semi-Lagrangian scheme, which, because it is formulated to be compatible with the continuity equation, has different forms for the horizontal and vertical directions. The horizontal form is an ordinary semi-Lagrangian scheme, in which departure point locations are calculated along the great circle by the method of Bates et al. (1990), using the cubic Lagrange interpolation for the velocity field. The vertical form, however, is equivalent to a mass-conserving flux-form in which transformed pressure coordinates are specified by the vertical velocity (Shibata et al., 2005). In this scheme, a transport calculation is used to find the departure mass of air or a chemical species in a transformed vertical ordinate. First, vertical ordinate transformations are performed separately, using vertical displacements integrated from the vertical velocity during a half time step, backward at arrival points and forward at departure points, and then horizontal wind fields on the resultant intermediate vertical ordinates are calculated at both arrival and departure points. Next, the departure point location and departure mass are calculated using a full time step from these two horizontal wind fields with an ordinary semi-Lagrangian scheme. Finally, the departure mass is vertically transformed back to the original pressure ordinate using a half time step.

However, the hybrid semi-Lagrangian transport scheme describes only the general formulation without specifying how to calculate air density or abundances of chemical species at horizontal departure points in the transformed vertical coordinates. The previous scheme (Cubic3) uses a cubic interpolation of neighboring abundances in the horizontal direction and also uses it for overhead column abundances in the vertical direction (Shibata et al., 2005). A new PRM5 scheme has been developed for the Cubic3 scheme; it improves both vertical and horizontal procedures to better simulate distributions of air mass and chemical constituents. The vertical procedure employs a piecewise rational method (PRM) (Xiao and Peng, 2004), and the horizontal procedure uses quintic interpolation. The PRM, which uses an analytically integrable rational function to reconstruct in-cell profiles from cell-averaged values, exhibits better performance for steeper-gradient profiles than the piecewise parabolic method (PPM) (Colella and Woodward, 1984), which uses a parabolic function. This improvement of the transport scheme led to substantial decreases in positive ozone biases, particularly in the tropical upper troposphere and lower stratosphere (not shown), and to a better representation of the tape-recorder effect of water vapor in the tropical stratosphere (Mote et al., 1996). Details of the PRM5 scheme and its impacts on the chemistry and dynamics are described by Shibata et al. (in preparation).

Since the vertical transport conserves mass owing to the nature of its flux-form, a correction for the mass conservation is made only for the horizontal transport, in which high-order interpolations are quintic and low-order interpolations are cubic (Gravel and Staniforth, 1994). The detailed formulation is given in Appendix-I. The time step of this transport scheme can be taken longer than that in the dynamics module because its critical time step is much longer than that required to satisfy the CFL condition for the finite difference scheme.

2.2.2 Coupling Among the Dynamics Module and the Transport and Chemistry Processes
The transport scheme uses the time-mean fields of the horizontal wind and its divergence, vertical wind, and surface pressure from the dynamics module (see Appendix I for details) to save computation time, although instantaneous fields are also usable. This means that the coupling between the dynamics module and the transport scheme is loose in time. That is, the chemistry module is called after the time integration of even steps in the dynamics module to reduce high-frequency components such as gravity waves. Similarly, the coupling between the transport and the chemistry schemes is also loose, because the time step in the chemistry scheme is fixed at 15 minutes to attain sufficient accuracy in iterative calculations. Radiatively active gases that provide feedback from the chemistry to the dynamics modules are O$_3$, N$_2$O and CH$_4$.

2.2.3 Homogeneous Reactions

HF-related species and reactions are incorporated into the previous chemistry module (Shibata et al., 1999), resulting in 36 long-lived species including seven families, and 15 short-lived species, with 80 gas-phase reactions. Three CFCs, two halons, methyl chloride, and methyl bromide are included as totally or partly anthropogenic gases. It should be noted that the chemistry module covers the whole model domain from the surface to approximately the mesopause, but does not include detailed processes for tropospheric chemistry. The names of species and definitions of families are listed in Table 1, and gas-phase reactions are listed in Table 2. Note that O($^3P$) and O($^1D$) are henceforth referred to simply as O and O$^1D$ unless otherwise specified. The rate constants data are from the Jet Propulsion Laboratory 2002 (JPL02) database compiled by Sander et al. (2003) except for $[hk_1: O + O + M \rightarrow O_2 + M]$ and $[a_{24}: H_2 + O \rightarrow OH + H]$, which are not included in JPL02. The rate constant of $hk_1$ is taken from the work of Brasseur and Offermann(1986) and that of $a_{24}$ from the work of Lefèvre et al. (1994).

Long-lived species are transported and are subject to time integration, the form of which differs for each species between daytime and nighttime (see Appendix II). This is because all photolysis rates are zero at night, and because some short-lived species are set to zero for the nighttime calculation of long-lived species.

Short-lived species are neither transported nor integrated, but are diagnosed at each time step; two different methods are used, depending on the family. For the HO$_x$ family and N, an instantaneous equilibrium condition is assumed (equilibrium method), whereas a reduced Jacobian method (Sandilands and McConnel, 1997) is used for other families (i.e., O$_x$, NO$_x$, ClO$_x$ and BrO$_x$). This method solves a linearized differential matrix equation of family members to obtain the partitioning ratio. There are two advantages to using the reduced Jacobian method. One is that all of the terms, even though some may be trivial, are considered, in distinct contrast to the equilibrium method, which, in principle, neglects all the terms irrelevant to the partitioning ratio. The other is that the sum of the time derivative of each member exactly coincides with that of the family, as shown below.

\[
\frac{d}{dt}[NO_x] = \frac{d}{dt}[NO] + \frac{d}{dt}[NO_2] + \frac{d}{dt}[NO_3].
\]

This equation does not hold true in the equilibrium method, because some terms on the right-hand side are forced to zero to obtain the partitioning ratio. It should be noted,
however, that the reduced Jacobian method is valid only when stiffness coefficients are
less than a certain range of values.

During nighttime a very small value ($1 \times 10^{-10}$ ppmv) or zero is set for chemical
species such as H, O($^1D$), O($^3P$), OH, HO$_2$, Cl, N, NO and Br, and the still-remaining
members of NO$_x$ (NO$_2$ and NO$_3$) and BrO$_x$ (i.e., BrO and BrCl) are solved by using
the reduced Jacobian method as during daytime. The diagnosed formulas of short-lived
species are given in Appendix III.

2.2.4 Photodissociation

The photolysis process includes 35 photodissociations (Table 3). The same subscript
number represents different pathways in Table 3. For example, both 10$_2$ and 33$_2$
represent the ClONO$_2$ photodissociation, but productions are different. For each chemical
species, the photolysis rate coefficient, which is a function of height, overhead column
ozone, solar zenith angle, and temperature, was calculated beforehand under conditions
of clear sky with a specified model ozone profile and a surface albedo of 0.3, and then
stored in a look-up table. The look-up table was created mainly on the basis of the
NCAR SOCRATES model (Huang et al., 1998), and a temperature effect was newly
incorporated into 16 photodissociations (marked with * in Table 3) that showed specific
temperature dependence in the quantum yield or the absorption cross section. The look-up
table database is taken from JPL02 for absorption cross section and quantum yield,
whereas Kockarts (1994) approximation is used for the oxygen Schumann-Runge bands
(175-205 nm). Figure 3 depicts the vertical profiles of the photolysis rate coefficients
for all 35 photodissociations at the 30° solar zenith angle for a standard ozone profile,
and Fig. 4 shows the relationship between the photolysis coefficients (expressed by their
base 10 exponents) and the solar zenith angle. Specifically, the secant of the solar zenith
angle (SZA), not the angle itself, is used as an argument in the photolysis look-up table
when $SZA < 65^\circ$, whereas the Chapman function is used instead for $65^\circ < SZA < 95^\circ$
to account for the sphericity of the Earth’s atmosphere, where 95° is the criterion used
do distinguish between daytime and nighttime. It should be noted that the Chapman
function coincides with the secant of the solar zenith angle for the plane-parallel atmo-
sphere. In MJ98-CCM the Chapman function is approximated by the simplified form
described by Smith and Smith (1972). Figure 5 depicts the relationship between the
solar zenith angle when the sphericity effect is not taken into account and that based
on the simplified Chapman function, which is nearly independent of height within the
vertical range of the current model top at 0.01 hPa. It is evident that the sphericity
effect is substantial when solar rays are nearly grazing the Earth’s surface, such as when
$SZA > 85^\circ$.

2.2.5 Heterogeneous Reactions

The following six heterogeneous reactions on PSCs are considered, and the reaction
probability data of JPL00 are used.
Two types of PSCs are included, similar to Chipperfield et al. (1993): type I PSCs composed of nitric acid trihydrate (NAT; HNO$_3$ · 3H$_2$O), and type II PSCs composed of water ice. The saturation vapor pressure of HNO$_3$ over NAT is calculated by the formula of Hanson and Mauersberger (1988). Type I PSCs are assumed to be composed of uniform particles with a radius of 1 $\mu$m and a sedimentation velocity of 0.015 km day$^{-1}$. In the conversion from mass to surface area, a constant NAT density of 1.35 (g cm$^{-3}$) is used. For type II PSCs, on the other hand, the formula of Murray (1967) is used to determine the saturation vapor pressure over ice. Type II PSCs are assumed to be composed of uniform particles with a radius of 10 $\mu$m, a sedimentation velocity of 1.5 km day$^{-1}$, and a constant density of 0.928 (g cm$^{-3}$).

The condensed HCl number density on PSCs is assumed to be proportional to those of HNO$_3$ and H$_2$O, and its formula is based on that of Hanson and Mauersberger (1990):

$$[HCl(s)] = 0.0035 \times [HNO_3(s)] + 0.0001 \times [H_2O(s)].$$

PSCs are assumed not to change their surface area within an iteration loop of time integration (for details, see 2.2.8 Time integration), thereby simplifying heterogeneous reaction rates by making them independent of the number densities of species, as for the homogeneous reactions. By this assumption HNO$_3$, H$_2$O, and HCl in PSCs are integrated only in the final iteration loop, because the heterogeneous reaction rates depend on the gas species around PSCs rather than the species contained in the PSCs. For simplicity, PSCs are not transported but evaporated, even if they are supersaturated after the sedimentation process. This resembles the treatment of diagnostic clouds in GCMs, in which water vapor is transported instead of clouds.

Three heterogeneous reactions ($g_1 - g_3$) on sulfate aerosols are also included. Sulfate aerosols in the stratosphere are treated as external conditions rather than prognostic variables because sulfur species are not included in the current version. Sulfate aerosols are thus not transported but are assumed to be composed a solution of about 75% H$_2$SO$_4$ in water.

$$g_1 \ ClONO_2 + (H_2O)_l \rightarrow HOCl + HNO_3$$
$$g_2 \ N_2O_5 + (H_2O)_l \rightarrow 2HNO_3$$
$$g_3 \ BrONO_2 + (H_2O)_l \rightarrow HOBr + HNO_3$$
At temperatures below about 200 K, sulfate aerosol particles absorb a significant amount of HNO$_3$, becoming ternary solutions of H$_2$SO$_4$/HNO$_3$/H$_2$O (e.g., Tabazadeh et al., 1994), and leading to the formation of PSC type I particles. That is, the H$_2$SO$_4$ concentration decreases below 200 K, and it decreases particularly rapidly below 195 K (e.g., Carslaw et al., 1994). To avoid the coexistence of sulfate aerosols with PSCs at very low temperatures, the surface area of sulfate aerosols is decreased by multiplying it by a temperature dependency factor that changes linearly with temperature from 1.0 at 200 K to 0.0 at 190 K.

2.2.6 Boundary Condition at the Surface

Abundances are specified, instead of fluxes being imposed, at the surface for the chemical species that originate naturally or anthropogenically at the surface. These species are N$_2$O, CH$_4$, CO$_2$, CO, NO$_y$, CCl$_4$, CFC$_3$, CF$_2$Cl$_2$, CH$_3$Cl, CH$_3$Br, CF$_2$ClBr, and CF$_3$Br. In addition, to represent the abundance of total chlorine atoms (CCl$_y$) in organic chlorine compounds, which include other chlorine-bearing species such as CF$_2$CCl$_3$, CH$_2$CCl$_3$, and CHF$_2$Cl in the real atmosphere, the abundances of CCl$_4$, CFC$_3$, CF$_2$Cl$_2$, and CH$_3$Cl are multiplied by a constant factor ($\alpha > 1$),

$$\alpha = \frac{[CCl_y]}{4[CCl_4] + 3[CFCl_3] + 2[CF_2Cl_2] + [CH_3Cl]},$$

where CF$_2$ClBr is omitted because of its minor abundance. In contrast, no such constraint is imposed on the abundance of total bromine atoms (CBr$_y$) in organic bromine compounds. N$_2$, O$_2$, and H$_2$ are assumed to be constant throughout the atmosphere and their volume mixing ratios are set to 0.78 $\times$ 10$^{-2}$, 0.21 $\times$ 10$^{-2}$, and 5 $\times$ 10$^{-7}$.

2.2.7 NO Sourced from Cosmic Rays

NO production by cosmic rays is incorporated following the method of Heaps (1978), as in SOCRATES (Huang et al., 1998). This production is particularly important in the polar nighttime mesosphere, where weak yet persistent subsidence brings NO$_x$-poor air from the upper atmosphere through transport, and the darkness switches off major NO$_x$ sources derived via photodissociation, resulting in very little NO$_x$ abundance. One ion pair exposed to the cosmic rays produces 1.3 NO molecules, and the production rate of NO from the model top (0.01 hPa) to the upper stratosphere of about 31 km (10 hPa) is expressed by

$$Q = 1.3(A + B\sin \theta^4)N (cm^{-3} s^{-1}),$$

where $\theta$ is the latitude, $A = 1.74 \times 10^{-18}$, $B = 2.84 \times 10^{-18}$, and $N$ is the total number density in molecules cm$^{-3}$. Note that $B$ is the value under maximum cosmic ray (solar minimum) conditions. The production rate below 31 km to the lower stratosphere of about 18 km (70 hPa) is similarly represented as

$$Q = 1.3(A + B\sin \theta^4)N_o^{1-n}N^n (cm^{-3} s^{-1}),$$

where $n = 0.6 + 0.8 \cos \theta$ and $N_o = 3.03 \times 10^{17}$, which is the reference number density at 31 km. Below the lower stratosphere the production rate is given as a linear function of altitude down to 8 km (about 300 hPa), where the production rate is fixed at 5 cm$^{-3}$ s$^{-1}$. 

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These equations are also applied in the polar cap regions, though they take a different form, described by Heaps(1978), in those regions.

2.2.8 Time Integration

The multiple implicit-explicit method (Jacobson, 1999) is used for the time integration with an iterative method that achieves both stability and mass conservation. That is, backward Euler integration is used for intermediate iteration loops

\[ q^{(n+1)}\Delta t = \frac{q^n\Delta t + \Delta t P}{1 + \Delta t L}, \]

where \( q^n\Delta t \) is the concentration at \( t = n\Delta t \), \( P \) is the production rate and \( L \) is the loss rate. Forward Euler integration, on the other hand, is applied to the final loop

\[ q^{(n+1)}\Delta t = q^n\Delta t + \Delta t P - \Delta t L, \]

to conserve mass. In the multiple implicit-explicit method, stability comes from the backward Euler integration, whereas mass conservation is due to the forward Euler integration. However, since the forward Euler integration does not ensure positive abundance as can be easily understood from its form, stabilized (converged) abundances are absolutely necessary in the final loop of the backward Euler integration. Usually, the time step is 15 minutes and there are five iteration loops.

2.2.9 Conservation and Negative Fill

Even though the forward Euler integration exactly conserves the mass of chemical species, it is apt to produce negative abundance when the time step is not sufficiently short, or when abundances at the previous iterative step are not near convergent conditions. Even if abundance is positive for each chemical species, mass conservation is sometimes violated in one family, such as \( Br_y \neq BrO_x + HBr + HOBr + BrONO_2 \). Such inconsistency or negative abundance is also triggered or induced by transport. When negative abundances are detected in a family, they are replaced with a specified minimum value, and, simultaneously, other positive abundances in the family are decreased to conserve the total mass of the family. That is, the sum of negative abundances is partitioned among the members of of the family with positive abundance in proportion to their abundances, as in TOMCAT CTM (Chipperfield, 1996). For a family \( A_y \) with \( m \) members \((A_1, A_2, ..., A_m)\), the following modifications are made sequentially:

\[ M^A_{total} = A_y, \]

\[ A'_i = Max(A_i, \delta), \]

\[ M^A_{posit} = \sum_{i=1}^{m} A'_i, \]

\[ A_i = A'_i \times \frac{M^A_{total}}{M^A_{posit}}. \]
where $\delta$ is a certain very small value, $1.0 \times 10^{-30}$ of the volume mixing ratio. It is evident that the abundances of the species of family $A_y$ are positively adjusted, whereas the total family abundance is kept unchanged.

A slightly different treatment is necessary when some members belong to two families simultaneously. For example, $BrCl$ is a member of both the $Br_y$ family and the $Cl_y$ family. In this case a conditional modification is required. Consider a family $B_y$ of $n$ members ($B_1, B_2, \ldots, B_{n-m}, A_1 B_{n-m+1}, \ldots, A_m B_n$), where $A_1 B_{n-m+1}, \ldots, A_m B_n$ belong to family $A_y$ and have already been corrected to be positive and to maintain mass conservation. Then,

$$M^B_{\text{total}} = B_y - \sum_{j=1}^{m} A_j B_{n-m+j}$$

$$B'_i = \text{Max}(B_i, \delta) \quad \text{for } i = 1, n - m$$

$$M^B_{\text{posit}} = \sum_{i=1}^{n-m} B'_i$$

if $M^B_{\text{total}} > 0$ then

$$B_i = B'_i \cdot (M^B_{\text{total}}/M^B_{\text{posit}}) \quad \text{for } i = 1, n - m$$

if $M^B_{\text{total}} \leq 0$ then

$$B_y = M^B_{\text{posit}} + \sum_{j=1}^{m} A_j B_{n-m+j}$$

This negative-fill is carried out to minimize the change in abundance by first adjusting the least abundant family and then the more abundant families, that is, in the order $Br_y, Cl_y$, and $NO_y$.

2.2.10 Vertical Diffusion and the Deposition Process

The turbulent mixing process is calculated by the same method as that used in the dynamics module, except for the lower boundary condition, where zero flux at the surface is assumed for all chemical species. Turbulent mixing is calculated last in one time step, following dry/wet depositions and the specification of abundances at the surface. Vertical mixing due to convection is not included in the current version, but will be implemented in the future.

Dry deposition is applied only for $O_x$ at the surface, using the dry deposition velocity of ozone (Brasseur et al., 1998), the magnitude of which depends on the surface conditions. It is $0.075 \text{ cm sec}^{-1}$ over ocean and sea ice, whereas the bare ground value
of 0.33 cm sec\(^{-1}\) is used over land, neglecting vegetation conditions. The wet deposition (in-cloud scavenging and rain-out) process is applied for water-soluble gases such as HNO\(_3\), HCl, HBr, and HF following Hough’s (1991) parameterization. The loss rate \(\beta_i(s^{-1})\) of water-soluble gas \(i\) is given by

\[
\beta_i = \frac{Pr}{(H_i \cdot d_{H_2O}) + Pr \Delta t},
\]

where \(d_{H_2O}(kgm^{-3})\) is the density of liquid water, \(\Delta t(s)\) is the time step, and \(Pr(kgm^{-3}s^{-1})\) is the sum of the convective and large-scale precipitation rates calculated in the dynamics module. \(H_i\) is the dimensionless Henry’s law coefficient expressed by

\[
H_i = \frac{273.15 \cdot p}{K_i \cdot 22.415 \cdot T \cdot p_0},
\]

where \(p(Pa)\) is the local pressure, \(p_0(Pa)\) is the standard surface pressure, and \(K_i(mol^{-1}atm^{-1})\) is the Henry’s law coefficients, \(3.3 \times 10^6\) for \(K_{HNO_3}\) and \(3.3 \times 10^5\) for \(K_{HCl}, K_{HBr},\) and \(K_{HF}\) (Huang et al., 1998). For temperatures below \(-15^\circ C\), it is assumed that all cloud droplets are frozen, causing wet deposition to be switched off.

2.3 Conditions for Simulation

Five members CCM integrations have been performed under the CCMVal REF1 scenario (Eyring et al., 2005), in which both natural and anthropogenic forcings of SST, sea ice, greenhouse gases, halogens, the 11-year solar cycle, and volcanic aerosols are given daily by interpolation from monthly mean values. The integration period is from the middle of 1979 to December 2004; before this, a spin-up integration was carried out covering about 10 years using 1970 conditions, following which time-varying conditions were used up to 1979 without the 11-year solar cycle and with constant background-level aerosols. The five members (PRM52 to PRM56) have different initial dates, and the time lags among them are one month. The general conditions of the REF1 are described by Eyring et al. (2005) and references therein, so only specific treatments of the forcings are described here. The SSTs taken from the UK Met Office Hadley Centre data (HadISST1) (Rayner et al., 2003), are corrected to retain temporal variability even when interpolated from monthly to daily values, similar to those used in Atmospheric Model Intercomparison Project (AMIP) II (Taylor et al., 2000). The concentrations of well-mixed GHGs (CO\(_2\), CH\(_4\), and N\(_2\)O), based on the Intergovernmental Panel on Climate Change (IPCC) data (2001), and those of halogens (CCl\(_4\), CFC\(_3\), CF\(_2\)Cl\(_2\), CH\(_3\)Cl, CH\(_3\)Br, CF\(_2\)ClBr, and CF\(_3\)Br), derived from World Meteorological Organization (WMO)/United Nations Environment Programme (UNEP) data (2003) and their extended data set through 2004, are specified at the surface. In addition, the abundances of CCl\(_4\), CFC\(_3\), CF\(_2\)Cl\(_2\), and CH\(_3\)Cl are multiplied by a factor \((\alpha)\) each month as stated before to represent the abundance of total chlorine atoms (CCl\(_y\)) in organic chlorine compounds in the real atmosphere. This factor is approximately 1.3, though it varies with the date. The 11-year solar cycle is given as irradiance data with a spectral resolution of 1 nm, which were used to create a look-up table for photodissociation, as described by Sekiyama et al. (2006), and solar fluxes of coarser spectral intervals for the radiative heating calculation. Figure 6 shows the relative changes (%) in the photolysis rate coefficients between the solar maximum and minimum for some
representative species (O₃, O₂, and H₂O), which strongly depend on solar irradiance variations. Volcanic aerosols are considered on the basis of the zonal-mean stratospheric aerosol optical depth at 0.55 µm and the effective radius, based on the work of Sato et al. (1993) and their extended data (http://data.giss.nasa.gov/modelforce/strataer), and from the surface-area densities (SADs) of sulfate aerosols, similar to those used by Jackman et al. (1996) and updated by D. B. Considine (NASA Langley Research Center) (Eyring et al., 2006). The integration period included two giant volcanic eruptions, El Chichón (7.4°N, 93.2°W) in March-April 1982 and Mount Pinatubo (15.1°N, 120.4°E) in June 1991. Figure 7 displays the evolution of the optical depth at 0.55µm and the effective radius from 1980 to 2004; the global extension of the aerosols owing to the two giant volcanic eruptions is clearly seen.
3. Climatology

3.1 Wind and Temperature

Climatological fields of seasonal- and zonal-mean zonal wind of the ERA-40 reanalysis data (Uppala et al., 2005) for the 1990s (10 years from 1990 to 1999) are illustrated in Fig. 8, and those of the simulated wind for each of the five members are depicted in Figs. 9a-e, together with the ensemble mean of the five members in Fig. 9f. Similarly, Figs. 10 and 11a-f show the seasonal- and zonal-mean temperatures. Even when ozone and other radiatively active gases are treated interactively, the overall features of observed wind and temperature (e.g., ERA-40; CIRA-86 (Fleming et al., 1990)) are more or less realistically reproduced, similar to those in most middle atmospheric GCMs (Pawson et al., 2000). It should be noted that ERA-40 consists of modeled data above the upper stratosphere, and not necessarily observed data, because the number of the observed data for the reanalysis became very small in the upper stratosphere and above.

During the northern winter (December to February) the subtropical jet is well reproduced, compared with observations (ERA-40), with respect to the core strength and extent in both hemispheres except for a deeper westerly wind region in the tropical upper troposphere, accompanied by a stronger equatorward extension of the westerly wind. Instead, the northward extension of the subtropical jet is underestimated at around 60°N. In the northern stratosphere, the separation between the subtropical jet and the polar night jet is not well simulated, as revealed by the significantly stronger wind than the observed (see the 20 ms$^{-1}$ contour) in the col between the two jets, arising from a cold bias in the polar lower stratosphere. In contrast, the polar upper stratosphere has a warm bias, resulting in a much weaker simulated polar night jet having a slighter equatorward tilt with altitude than the observed. This underestimated polar night jet stems from stronger wave activities, which are initiated by a stronger GWD and amplified by a wave-mean flow interaction, causing overestimation of the poleward ozone transport, as described later. The easterly wind in the northern high-latitude mesosphere is due solely to the GWD, yielding a clear equatorward tilt of the polar night jet above the stratopause. Coincident with the poor separation of the two jets in the winter hemisphere, there appears to be an upward extension of the subtropical jet in the summer hemisphere, leading to an upward shift of the zero-wind altitude in southern high latitudes. Interannual variations of the polar night jet are much larger in the simulation than in the observation data in the upper stratosphere, where the simulated polar night jet is weaker than the observed. Interannual variations among the members are also large: those of two members are smaller than those of the other three. However, the strength of the polar night jet itself is not related to the interannual variations but to the lower stratospheric temperature in northern high latitudes.

During the southern winter (June to August), the southern subtropical jet has a stronger equatorward and weaker poleward extension, similar to the northern subtropical jet during the northern winter. The polar night jet is more or less realistically reproduced above the middle stratosphere owing to the weak wave activities in the Southern Hemisphere, whereas it is overestimated with a cold bias in the lower stratosphere, and the separation from the subtropical jet is less clear than in the observation data. Interannual variations of the polar night jet are smaller in the simulation than the observation. There appears to be a mesospheric easterly wind at southern high latitudes, similar to that during December to February at northern high latitudes, but the
magnitude of the former is twice \((60 \, m/s)\) that of the latter, reflecting the difference in the vertical wind profiles below the middle mesosphere. The summer subtropical jet in the Northern Hemisphere is well simulated with the zero-wind line being almost at the observed altitude, in contrast to that during December to February in the Southern Hemisphere.

The seasonal march from winter to spring is known to be retarded, by about one month, in the simulation compared with the observation data (Shibata et al., 2005), causing the simulated polar night jet to be stronger than the observed during the southern spring (September to November) in the Southern Hemisphere and the stratospheric westerly wind to be stronger during the northern spring (March to May) in the northern high latitudes. Conversely, the stratospheric westerly wind during autumn is weaker in the simulation than in the observation data in both hemispheres (Figs. 8 and 9).

3.2 Ozone

Climatological fields of the observed seasonal- and zonal-mean ozone volume mixing ratio in the middle atmosphere for the 1990s are illustrated in Fig. 12, and those of the simulated ozone are depicted in Figs. 13a-e, together with the ensemble mean of the five members in Fig. 13f. The observed ozone is taken from satellite measurements by the total ozone mapping spectrometer (TOMS) and solar backscattered ultraviolet (SBUV), that is, the TOMS/SBUV merged total and profile ozone data sets based on the version 8 retrieval algorithm (http://code916.gsfc.nasa.gov/Data_services/merged).

Though the models qualitatively reproduce the ozone core region in the equatorial upper stratosphere centered at 10 hPa, quantitatively they slightly underestimate, by about 1 ppmv, for the observed peak value of 9-10 ppmv. Still, the models succeed in simulating the representative area of the ozone core encircled by an 8-ppmv contour. In the extratropics, on the other hand, a poleward extension of the high ozone area from the ozone core below the middle stratosphere can be seen in the simulation during all seasons, resulting in a positive bias in total ozone, particularly at high latitudes.

The simulated and observed seasonal climatological march of the zonal-mean total ozone in the 1990s is depicted as a function of months in Fig. 14. The model reproduced the overall seasonal evolution of total ozone but exhibited positive biases everywhere. The relatively high positive biases at northern high latitudes and in southern mid-latitudes from winter to spring in each hemisphere stem from the overestimated poleward ozone transport. In terms of annual mean values, the positive biases are slightly less than 20 DU in the tropics and reach 20 to 40 DU in the extratropics of both hemispheres (not shown). Interannual variations of the simulated annual-mean total ozone are about 6 DU in the tropics, 10 DU in the northern latitudes, and 16 DU in the southern high latitudes, whereas the corresponding observed values are 2, 4, and 3 DU. Note that the observed values at high latitudes are calculated from those days when TOMS measurements were made. The simulated extratropical total ozone in the Northern Hemisphere peaks in April/May, about one month later than in the observation data, because the simulated transition in dynamics from winter to spring (that is, from westerly to easterly winds) is retarded by about one month in the stratosphere as stated before. In contrast, the minimum total ozone appears in September, as in the observation data. In the tropics, the minimum axis of the simulated total ozone crosses the equator from north to south in mid-winter and then from south to north in mid-summer, unlike in the observed data,
when these events occur in the months around the spring and autumnal equinoxes. In the southern extratropics, the simulated maximum total ozone appears at around 50°S from July to November, and the ozone hole occurs inside a strong and persistent polar vortex in October/November, about one month later than in the observations. This time lag is due to the simulated polar vortex being much deeper than the observed, thus retarding the seasonal change from winter to spring by about one month, as in the Northern Hemisphere.

The time evolution of total ozone for the entire period (1980 to 2004) is displayed in Fig. 15, together with the observed (TOMS/SBUV) total ozone for 1980 to 2001. The model simulates larger interannual variations in the northern high latitudes than in the southern high latitudes, similar to the observation data. The simulated ozone hole area increases in size from year to year beginning in the early 1980s and eventually stabilizes, beginning in the late 1990s. Quantitatively, however, the model significantly underestimates the maximum area of the ozone hole until the late 1990s, whereas the simulated minimum total ozone quantitatively coincides well with the observation data (Fig. 16). It is evident that the simulated total ozone exhibits prominent decreasing trends in both the extratropics of both hemispheres and the tropics, whereas the observation data show no decreasing trend in the tropics (e.g., Fioletov et al., 2002). The details of the trend are described below on the basis of a multiple linear regression analysis.

3.3 QBO

Figure 17 depicts the observed equatorial zonal-mean zonal wind and temperature averaged from 5°S to 5°N, and ozone averaged from 10°S to 10°N. These data have been deseasonalized by subtracting the observed long-term monthly means. The observed ozone is based on the Halogen Occultation Experiment (HALOE) data (Russell et al., 1993). Figures 18 to 20 illustrate those parameters for each of the five members of the simulation. This version of the MRI-CCM also reproduced the QBO in zonal wind, temperature, and ozone with its features being very similar to those of the previous version (Shibata and Deushi, 2005b) simulated under annually repeating forcings, except in the periods after the two major volcanic eruptions, when strong warmings at about 50 hPa and substantial ozone decreases at around 20 hPa are evident (Figs. 19 and 20).

When the same e-folding time profile as in the previous version was used for the horizontal diffusion, the QBO period became much shorter (about 20 months) than the previous value of 31 months through a substantial decrease in the ozone positive bias in the tropical lower stratosphere (not shown), arising from the improvement in the transport scheme for chemical constituents. This shortening of the QBO period can be ascribed to a decrease in the solar heating feedback of ozone because the terrestrial radiation of ozone plays a minor role in the QBO heating budget (Shibata and Deushi, 2005b). The quantitative relationship between the ozone feedback and the QBO period will be described in another paper (Shibata et al., in preparation).

To prolong the QBO period to a realistic value, the horizontal diffusion is weakened (that is, the e-folding time of the horizontal diffusion is decreased to about a half in the middle atmosphere), resulting in a QBO period of 27 months (Figs. 18-20). Though in the stratosphere the simulated QBO amplitude of the zonal wind is smaller than that in the observation data, similar to the QBOs simulated by other three-dimensional models (e.g., Takahashi, 1999; Butchart et al., 2003; Giorgetta et al., 2006), the simulated
QBO still has some of the observed features: stalling sometimes occurs during the descent of the westward wind; the amplitude of zonal wind peaks at 20 hPa; vertical wind shear is stronger during eastward than during westward acceleration; and the duration of the eastward wind is longer than that of the westward wind below about 50 hPa (e.g., Baldwin et al., 2001; Pascoe et al., 2005). The simulated ozone QBO also captures observed characteristics such as the amplitude peaking at 30 to 40 hPa and diminishing rapidly below 50 hPa (e.g., Randel and Wu, 1996; Logan et al., 2003). The lag correlation between ozone and zonal wind reveals that the phase of the ozone QBO precedes that of the zonal wind QBO by about a quarter cycle below 20 hPa (not shown), as it does in the observation data (Hasebe, 1994).

In the upper stratosphere, however, the simulated QBO amplitudes of zonal wind, temperature, and ozone are larger than in the observation data, particularly above 5 hPa, as in the previous version (Shibata and Deushi, 2005b). In contrast, the ozone QBO at about 10 hPa is underestimated in the simulation, with the result that the vertical structure of double peaks with alternating signs is not necessarily well reproduced in the simulation. In addition, a decreasing trend is evident in the upper stratosphere of the simulated ozone (not shown), whereas no such trend is seen in the observation data or in the simulated zonal wind. This decreasing trend in the simulated ozone is also statistically significant below the middle stratosphere, as will be described later.

Figure 21 displays the power spectrum of the equatorial zonal-mean zonal wind averaged between 10°S and 10°N for the simulation and the observation data (ERA-40). The observed semianual components show large power values above 10 hPa in the upper stratosphere, where the power increases with altitude and peaks near the stratopause. The observed semianual components also show a certain power in the 100-200 hPa region of the upper troposphere. The annual components show a certain power near the surface, in the upper troposphere, and in the stratosphere, in which the power increases with altitude and reaches a maximum at around the stratopause, similar to the semianual component. These features of the observed semianual and annual components are well reproduced in the simulation with very small variations among the members.

The simulated QBO has a period of 27 months with a maximum at 20 hPa in all members; this is very similar to the observed period (28 months) and maximum altitude. However, the simulated QBO power is underestimated as about 80% of the observed QBO power. The variations in the QBO power among the members are larger than those of the semianual and annual components.

It should be noted that the simulated QBO phases are very different from the observed QBO phase, owing to the differences in the initial fields and periods, as can readily be seen from Figs. 17 and 18. Likewise, the simulated QBO phase relation with the seasonal cycle is different from the observation data. Thus, the atmospheric and chemistry responses to the imposed forcings may differ from the observed responses, not only in the tropics but also in the extratropics, because of differences in the mean meridional circulation (e.g., Plumb and Bell, 1982) associated with the QBO, even if the various observed forcings are used.
4. Specific Signals in the Regression Analysis

Multiple linear regression analysis was used to isolate specific signals from the zonal-mean anomalies in temperature, zonal wind, and ozone data for the simulation and observation data (e.g., Randel and Cobb, 1994; Bodeker et al., 2001). Reference (explanatory) variables were the mean value, the linear trend, the QBOs at 20 and 50 hPa, volcanic aerosols of El Chichón and Mount Pinatubo, ENSO, and the 11-year solar cycle. Thus, the regression model for ozone is

\[
O_3(t) = A + B \times t + C \times QBO^{50\text{hPa}}(t) + D \times QBO^{20\text{hPa}}(t) \\
+ E \times \text{El Chichón}(t - \alpha) + F \times \text{Pinatubo}(t - \beta) \\
+ G \times \text{ENSO}(t) + H \times \text{Solar Flux}(t) \\
+ \text{Residual}(t),
\]

and likewise for temperature, where \(\alpha\) and \(\beta\) are time lags (in months) of less than, or equal to, 12. Coefficients A through G (referred to as signals henceforth) are expanded by annual, semiannual, and triannual cycles to explain seasonality.

\[
A = a_0 + a_1 \cos(wt) + b_1 \sin(wt) + a_2 \cos(2wt) + b_2 \sin(2wt) + a_3 \cos(3wt) + b_3 \sin(3wt),
\]

\[
w = \frac{2\pi}{12\text{ months}}.
\]

The QBO reference terms are taken from the zonal-mean zonal winds over the equator at 20 and 50 hPa (henceforth referred to as QBO20 and QBO50). It should be noted that QBO20 and QBO50 are not completely orthogonal (a quarter cycle apart) but approximately so, in both the simulation and the ERA-40 data set (not shown), and are similar to the time series of the QBO empirical orthogonal functions (EOFs) 1 and 2 (e.g., Crooks and Gray, 2005; Stolarski et al., 2006). The volcanic reference terms are the global-mean optical depths at 0.55 \(\mu\)m, with time lags \(a\) and \(b\) representing the delayed responses of ozone and temperature. The time lags \(\alpha\) and \(\beta\) are so calculated that the correlation between the regressed data and target data is largest at each point for \(\alpha \leq 12\) and \(\beta \leq 12\). The ENSO reference term is the Southern Oscillation Index (SOI), and the solar reference term is the 10.7 cm radio flux (F10.7) in solar units \((10^{-22}Wm^{-2}Hz^{-1})\).

The coefficients in the regression model are calculated by the least-squares method against deseasonalized monthly mean data, which are set to zero for periods for which ozone observation data are missing. The residual term, which regulates the fitting, was found to be sufficiently small to assure the validity of the current regression model. For example, for the zonal mean temperature, the ratio of the variances of the regressed data and target data exceeds 0.55 in the stratosphere between approximately 40°S and 50°N in the simulation and between 40°S and 40°N in the ERA-40 data set. Since the square root of the ratio is the correlation coefficient between the regressed data and the target data, a ratio of 0.55 corresponds to a correlation coefficient of 0.74. In addition, the regression model can explain the ozone variance better than the temperature variance in the stratosphere for both the simulation and observation data (SBUV), as found by Randel and Cobb (1994).
The regression results of the models require some attention. Sensitivity testing of the trend term (Bojkov et al., 1990; SPARC, 1998) demonstrated that the trend term is relatively insensitive; that is, it changes by about 10% in response to the inclusion or exclusion of the QBO, solar and other terms, as long as the time series is sufficiently longer than the 11-year solar cycle (SPARC, 1998). The trend standard errors, however, might be sensitive. The time series of the current analysis covers approximately two 11-year solar cycles for both the CCM simulation (25 years) and the ERA-40 data set (22 years), so the trend signal is expected to be valid for these two data sets. The ozone trend signal is also roughly valid in the tropics and mid-latitudes (between 60°S and 60°N), where data from a 20-year period are used. However, the trend signal derived in this study differs from those based on different regression models, as will be described later, because a multiple linear regression analysis does not necessarily yield unique signals. Different signals could be obtained from different reference sets, because some of the reference variables are not orthogonal to each other.

4.1 Trend

Figure 22a displays the linear trend (K/decade) of the annual- and zonal-mean temperature between 90°S and 90°N for the five members of the simulation, and Fig. 22b depicts the ensemble-mean trend and observed trend (ERA-40). All of the members reproduce the statistically significant cooling trend throughout the mid- and low-latitudes in the stratosphere and mesosphere, with maximum cooling exceeding 2.0 K/decade just below the stratopause. Though the maximum cooling areas differs from one member to another, the ensemble mean produces a strong cooling band from 60°S to 60°N, with two maxima exceeding 2.0 K/decade centered at 30°S and 30°N. Another statistically significant cooling trend can also be seen in the southern polar region below 10 hPa, particularly in the lower stratosphere, where the cooling reaches about 1.8 K/decade. In contrast, the ERA-40 data show a statistically significant cooling trend that occupies a narrower meridional band, from approximately 40°S to 40°N in the upper stratosphere, which extends downward and poleward to about 60°N in the northern lower stratosphere. The maximum cooling at the stratopause is approximately 2.5 K/decade—very similar to that in the simulation. However, some satellite observations reveal a somewhat different trend pattern, particularly poleward of 40° in both hemispheres, although the maximum cooling at the stratopause is of the same magnitude. The combined data sets of the Stratospheric Sounding Unit (SSU)/Microwave Sounding Unit (MSU) indicate statistically significant cooling above 40 km (3 hPa) extending from 70°S to 65°N in the upper stratosphere with interhemispheric symmetry and another statistically significant cooling trend in the extratropics (20° to 60°N and 20° to 60°S) of about 0.4 to 0.8 K/decade in the lower stratosphere below a relative minimum cooling in the middle stratosphere (around 30 to 35 km) (WMO/UNEP, 2003).

Figure 23 depicts the linear trend (%/decade) of the annual- and zonal-mean ozone levels between 90°S and 90°N for the simulation and two observation data sets. One observation data set is TOMS/SBUV and the other is taken from reconstructed data from the Stratospheric Aerosol and Gas Experiment (SAGE I and II) (McCormick et al., 1989) data set, with a multiple linear regression model using the decadal trend, solar cycle, and EOF1 and 2 of the QBO (Randel and Wu, 2007) as reference variables. The simulation reproduced the SAGE I/II observed features of a latitudinally symmetric
decreasing ozone trend with negative maxima in the extratropical upper stratosphere (2 to 5 hPa), and a third maximum in the tropical lower stratosphere (50 to 100 hPa), and a minimum (or positive) in between (25 hPa) in the tropics (e.g., WMO/UNEP, 2003; Newchurch et al., 2003; Randel and Wu, 2007), although the observed trends from SAGE I/II do not necessarily agree quantitatively with each other, depending on the analysis period and method. The simulated maxima in the extratropical upper stratosphere of -12%/decade are twice as large as the observed values of -6 to -8 %/decade. In contrast, the simulated third maximum of -2%/decade in the tropics is one-third of the observed trend of -6%/decade. These two observed maximum amplitudes in Fig. 23 are analyzed as larger values of -12 and -8%/decade for 1979 to 2005 by Randel and Wu (2007). This discrepancy results from the difference in the reference variables of the multiple linear regression models, as stated before.

Figure 24 plots the linear trend (DU/year) of the zonal-mean total ozone as a function of month between 90°S and 90°N for the simulation and observation data (TOMS/SBUV). The simulation captured the observed major characteristics of the severest total ozone depletion associated with the ozone hole in southern high latitudes during late winter (September) to early summer (December), and the second maximum ozone decrease in northern high latitudes during early spring, March to April, although the simulation somewhat overestimated the values. In contrast, the model calculated a persistent total ozone decrease in the tropics throughout the year, similar to a small but significant negative annual mean trend found in a CTM simulation (Stolarski et al., 2006), in conspicuous contrast to the observed (TOMS/SBUV) near-zero values. However, as pointed out by Randel and Wu (2007), the trend based on TOMS/SBUV data might reflect a tropospheric positive ozone trend canceling a stratospheric negative trend because the vertically integrated column ozone from SAGE I/II does exhibit a significant decrease of 8 DU from 1979 to 2005 in the tropics. If this is true, the simulated weak but significant negative trend in the tropics well reproduced the observed stratospheric ozone decrease because the model does not include detailed tropospheric chemistry.

4.2 QBO Signals

In the observed total ozone data (Fig. 25), positive values of the QBO20 signal cover the equatorial region from approximately 10°S to 10°N, with a slight peak in October/November. In the extratropics, negative (out-of-phase) values with maxima of the same magnitude as the equatorial signal extend in the mid-latitudes of both hemispheres during the winter-spring season in each hemisphere, March in the Northern Hemisphere and August/September in the Southern Hemisphere. These features are very similar to those regressed to the QBO 30 hPa wind (Randel and Cobb, 1994) or to the vertically weighted QBO wind with a peak at 20 hPa (Randel et al., 1995).

The simulation qualitatively reproduced the observed features with similar magnitudes, but the locations or dates of maxima are skewed and the mid-latitude negative values during the winter-spring season do not extend to the southern high latitudes in the winter hemisphere, unlike in the observation data (e.g., Randel and Cobb, 1994) or in a mechanistic chemistry model simulation (Kinnersley and Tung, 1999). In the simulation, a maximum appears in April/May in the equatorial region, with a weak second maximum in December, whereas a weak minimum appears in September. The
northern mid-latitude negative maximum occurs at around 40°N in February/March similarly to the observed one. The southern mid-latitude negative maximum appears at around 35°S in August/September, similarly to, and about 5°S equatorward of, the observed one. The month of the maximum total ozone in the equatorial region varies greatly among the members, whereas the timing of the mid-latitude negative maximum in the winter hemisphere varies very little.

The simulated QBO50 total ozone signal (Fig. 26) has statistically significant values in the tropics, where seasonal variations in the ensemble mean are very small, whereas the observed data show no statistically significant values in the tropics. This feature of the simulation is consistent with the ozone signals in the lowermost stratosphere, where the simulated ozone has a large positive signal (Fig. 32), as will be discussed later. Statistically significant and negative (out-of-phase) minima appear in the extratropics in the observed data two months behind the QBO20 ozone minimum signals in both hemispheres. All of the members approximately reproduced this feature, though the magnitude differed greatly among them. In addition, some members show statistically significant signals in high latitudes of both hemispheres.

The meridional structure of the simulated annual mean QBO20 wind signals are shown together with the observation data in Fig. 27. The simulated QBO20 wind signal has a vertical three-cell structure of alternating sign extending to the mesosphere, with a positive cell from 50 to 10 hPa, a negative cell above 0.8 hPa, and another positive cell above that in the mesosphere. Though the vertical extent of the positive cell centered at 20 hPa is slightly smaller, the simulated signal in the stratosphere agrees well with the observed stratospheric two-cell structure, the vertical profile of which is very similar to the QBO weight profile yielding the best fit to the total ozone QBO (Randel et al., 1995). The signal peaks over the equator and is latitudinally symmetric, with half-widths of about 20° in the stratosphere. The QBO50 zonal wind signal (Fig. 28) has a similar but vertically phase-shifted three-cell structure with a negative cell from 20 to 2 hPa and positive cells below and above this range. It is qualitatively in good agreement with the observed three-cell signal in the stratosphere, though the observed signal shows only the peripheral part of the uppermost positive cell between 2 and 1 hPa. It should be noted that the peak values of the QBO50 signal are approximately twice as large as those of the QBO20 signal in the simulation, and the QBO50 reference amplitude is about half the QBO20 reference amplitude (not shown). As a result, the product of the signal and reference is of similar magnitude in the multiple linear regression model (Eq. (1)). Also, the ratio of the reference amplitudes (QBO20/QBO50) in the observations is about two, and the ratio of the signal amplitude is about 0.8 for the positive cells and 0.4 for the negative cells. Thus, the products of the signal and reference are of approximately the same magnitude for the negative cells but are much larger for QBO20 than for QBO50.

The QBO signals of QBO20 and QBO50 zonal wind exhibit a wider latitudinal extent in the mesosphere (half-width, about 30°) than in the stratosphere (about 20°), coinciding with satellite measurements by the high-resolution Doppler imager (HRDI) on the Upper Atmosphere Research Satellite (UARS) (Burrage et al., 1996). There is also a slight hint of this above 2 hPa in the QBO50 zonal wind signal (Fig. 28) of ERA-40, which is available up to 1 hPa. A similar feature is just visible in an analysis using a ERA-40 data set that includes altitudes up to 0.1 hPa (Crooks and Gray, 2005), in which the QBO references are QBO EOF 1 and 2. Although the QBO amplitude
in the mesosphere is barely discernible and diminishes monotonically with altitude in the ERA-40 data set (Baldwin and Gray, 2005; Pascoe et al., 2005), the mesospheric QBO distinctly appeared in MRI-CCM simulation and is analyzed by multiple linear regression. A similarly clear mesospheric QBO has been simulated in a high-vertical-resolution version of MAECHAM5 GCM (Giorgetta et al., 2006).

Figures 29 and 30 depict the simulated and observed annual-mean QBO20 and QBO50 temperature signals, both of which peak over the equator with latitudinal symmetry (Crooks and Gray, 2005), similarly to the wind signals (Figs. 27 and 28). In the equatorial region, the latitudinal extents of the temperature signals are narrower than those of the wind signals, with half-widths of about 15° in the stratosphere and 20° in the mesosphere. The QBO20 temperature signals have a three-cell structure (Crooks and Gray, 2005) very similar to that of the QBO50 wind signals, whereas the QBO50 temperature signal has a four-cell structure, with a positive cell from below 100 to 30 hPa, a negative cell to 7 hPa, another positive cell to 0.3 hPa, and another negative cell above that.

The extratropical QBO temperature signals are out of phase with the tropical QBO signals in both hemispheres. These extratropical QBO signals arise from the secondary meridional circulation induced by the main equatorial QBO (e.g., Plumb and Bell, 1982) and are seen preferentially in the winter hemisphere (e.g., Randel et al., 1999), where the Brewer-Dobson circulation is much stronger than in the summer hemisphere, though the extratropical QBO signal in the winter hemisphere is not always present year around, but disappears in some winters (Randel et al., 1999). Thus, the latitudinal symmetry in the extratropical QBO temperature signal (Figs. 29 and 30) does not reflect reality but is a virtual structure resulting from the use of the annual mean.

The simulated annual-mean QBO20 ozone signal (Fig. 31) exhibits a four-cell structure over the equatorial region: a negative cell up to 60 hPa, another positive cell up to 20 hPa, another positive cell up to 2 hPa, and another negative cell above that. Since the pressure level of about 20 hPa corresponds to a critical altitude separating the photochemistry control region above from the transport control region below (e.g., Hasebe, 1994), the positive QBO20 ozone signal below 20 hPa is consistent with the positive QBO20 temperature signal, both of which are carried by a downdraft associated with the QBO westerly shear zone. Extratropical negative signals in temperature and ozone are also consistent with each other because an updraft acts as the return arm of the equatorial QBO in each hemisphere. In contrast, the positive QBO20 ozone signal above 20 hPa in the stratosphere can be interpreted as a response to the cooling (Ling and London, 1986) or to the transport of NOx-poor air (Chipperfield et al, 1994). In the simulation, the QBO20 temperature signal, for example (Fig. 29), exhibits a major cooling peak of about 1.4 K/(10m/s) and the QBO20 NOx signal (not shown) shows a very weak, reduced peak of about $0.3 \times 10^{-2} \text{ ppbv/(10m/s)}$ at 10 hPa. Detail analysis of this phenomenon, however, is beyond the scope of this paper. The simulated QBO20 ozone signal of the two positive cells below 3 hPa qualitatively agrees with the observation data (SBUV/TOMS), although the minimum value in the col between them is too low in the simulation.

The simulated annual mean QBO50 ozone signal (Fig. 32), which has a four-cell structure in the equatorial stratosphere, qualitatively agrees with the observed signal, which shows a negative cell centered around 3 hPa, a positive cell centered at 10 hPa,
and a negative cell centered around 30 hPa, although the lowest one is not statistically significant. However, the simulated positive cell below 30 hPa, with the largest magnitude centered at 70 hPa in the equatorial lower stratosphere, cannot be seen in TOMS/SBUV data, although there are no data below 50 hPa. As will be described below, this intensive positive cell in the lowermost stratosphere in the simulation is the cause of a significantly large response of total ozone in the equatorial region, whereas almost no response can be seen in the observed data.

4.3 Solar Signals

Figure 33 depicts the annual mean solar temperature signals in K per 100 solar units from 200 to 0.1 hPa between 90°S and 90°N for the simulation and observation data (ERA-40). Note that the values in Fig. 33 should be multiplied by 1.3 to obtain the differences between solar maximum and minimum, because the 130 F10.7 solar units correspond, on average, to the difference between the solar maximum and minimum. The ensemble mean of the simulation shows strong warming, exceeding 0.5 K around the stratopause from 60°S to 60°N, with maximum warming of 0.8 K and 0.7 K at 30°S and 30°N. The strong warming in mid-latitudes extends to the north pole at the same altitude and to the south pole with increasing altitude to about 0.1 hPa. On the other hand, a minimum warming can be seen from 30°S to 30°N around 5 hPa, with an upward bulge over the equator. Below this minimum warming, a lower stratospheric warming occupies the altitudes from 20 to 80 hPa and extends with latitudinal symmetry from about 40°S to 40°N, with a peak of 0.7 K at about 70 hPa. The lower stratospheric warming is probably due to the dynamics, because the UV impact scarcely penetrates down into the middle stratosphere (Shibata and Kodera, 2005). Variations among the members are not very large in the mid- and low latitudes, but one member is very different from the others in that there is no upward bulge in the tropical upper stratosphere and the tropical lower stratosphere warming is very shallow.

The observed annual mean solar temperature signal also has two extreme warming altitudes and a minimum warming altitude in between with latitudinal symmetry. The maximum warming signal area is between 1 and 5 hPa from 30°S to 30°N, with a peak of 1.4 K at 3 hPa around 15°N. The second maximum appears in the lower stratosphere, extending from 30°S to 30°N.

Satellite measurements or other upper-air observations do not cover a long enough period to stably and accurately analyze the 11-year solar cycle, but they include barely two cycles in total. As a result, the solar signal is detected differently, depending on the analysis methods or conditions employed (e.g., Scaife et al., 2000; Labitzke et al., 2002; Hood, 2004; Crooks and Gray, 2005). Even though they used ERA-40 data with a multiple linear regression analysis, the resultant solar temperature signal reported by Crooks and Gray (2005) differs, particularly in the tropical lower stratosphere, from that in this study. This difference is because some of the reference terms are not equivalent between the two analyses.

Figure 34 depicts the annual mean solar ozone signals in percent per 100 solar units between 90°S and 90°N for the simulation and the TOMS/SBUV and SAGE I/II observation data sets. The simulation reproduced two areas of strong ozone increases area over the tropics: one extends from 80°S to 60°N with a peak of about 2.8% at around 3 hPa and the other occupies a narrower latitudinal band, from 30°S to 30°N, with
4. Specific Signals in the Regression Analysis

a peak of about 3.6% at around 70 hPa. Thus, there is a minimum ozone increase area at around 20 hPa in between the two strong warmings. The ozone decrease in the mesosphere above 0.05 hPa results from an HOx increase, which is caused by the H$_2$O photodissociation due to a Lyman $\alpha$ increase.

These two areas of strong ozone increases are also seen in the observation data, although the two observation data sets show different detailed features. The upper stratospheric ozone increase altitude is just above the stratopause in the TOMS/SBUV data set, whereas it is at about 3 hPa in the SAGE I/II, similar to the simulation. The lower stratospheric ozone increase, on the other hand, peak at nearly the same altitude of 50 hPa in both data sets. Note that the negative signal can also be analyzed in the TOMS/SBUV and SAGE data (Lee and Smith, 2003; Hood, 2004; Randel and Wu, 2007), but the statistical significance is low in both satellite data sets (Hood, 2004; Randel and Wu, 2007).

It is worthwhile to point out that, like other CCMs (e.g., Tourpali et al., 2003; Egorova et al., 2004), MRI-CCM simulates a statistically significant 2 to 3% increase in annual mean ozone at about 3 hPa (not shown) without any maximum increase in the lower stratosphere in the difference between solar maximum and minimum time-slice runs, indicating that the upper stratospheric ozone increase is simply a response to the increase in UV irradiance.

4.4 ENSO Signals

Figure 35 illustrates the latitude-pressure cross section of the annual average ENSO signal of zonal-mean zonal wind ((m/s) per -1 standard deviation of the SOI) from 1000 to 1 hPa for the simulation and observation (ERA-40). The tropospheric response occurs mainly in the subtropics, peaking at about 25$^\circ$S and 25$^\circ$N (Crooks and Gray, 2005). Intensification of the subtropical jet thus occurs on the equatorward flank in both hemispheres and is approximately in thermal wind balance with the ENSO temperature signal, as described below. The CCM reproduced the subtropical jet response with regard to its strength and extent, though both quantities are somewhat underestimated. However, there are large discrepancies between the simulated and the observed signals in the tropical stratosphere. The cause may be interference between QBO and ENSO through aliasing in the multiple linear regression model (Crooks and Gray, 2005).

Figure 36 depicts the latitude-pressure cross section of the annual average ENSO signals of zonal-mean temperature (K per -1 standard deviation of the SOI) from 1000 to 1 hPa for the simulation and observations. ENSO is a coupled ocean-atmosphere fluctuation with east-west seasing of SST between the eastern and western tropical Pacific Ocean. SST in the eastern tropical Pacific rises by 1 to 2 K above normal during an El Niño warm event and decreases by a similar amount below normal during a La Niña cold event (e.g., Philander, 1989). In addition, ENSO possesses strong seasonality, with the atmospheric response being largest during the northern winter, though it can be seen in other seasons. The zonal-mean component with annual averaging (Figs. 35a and 35b) is thus smaller than the non-zonal component during the mature stage. The tropical tropospheric warming during El Niño is due to the latent heat release that results from enhanced convective activity. The cooling below the middle stratosphere in the tropics (Reid, 1994; Crooks and Gray, 2005) is due to an enhanced updraft (not shown), whereas the mid-latitude, warming in the 20 to 150 hPa region, centered around
35°S and 35°N, is caused by an enhanced downdraft (not shown). The CCM reproduced well the spatial pattern of the tropospheric warming and the stratospheric cooling in the tropics, though the amplitudes are about half the observed ones. The mid-latitude stratospheric values in the simulation are slightly larger than the observed values.

Figure 37 illustrates the latitude-pressure cross section of the annual average ENSO signal of zonal-mean ozone from 200 to 1 hPa for the simulation and observation data (TOMS/SBUV). As a result of the enhanced updraft in the tropics and the corresponding downdraft in the mid-latitudes of both hemispheres, there is an ozone decrease in the tropics and an ozone increase in the mid-latitudes, centered at 35°S and 35°N, in both the simulation and the observation data. It should be noted that the ozone decrease in the tropics occupies a vertically thicker region below 15 hPa than the cooling below 50 hPa and that it is latitudinally asymmetric, in contrast to the symmetric cooling.

4.5 Volcanic Signals

Figure 38 displays the evolution of the simulated global (65°S to 65°N) volcanic temperature signals for about a half year before and about three and a half years after the El Chichón eruption, along with the observed signals (ERA-40). The model reproduced the warming due to El Chichón volcanic aerosols qualitatively well with respect to its timing and extent until the middle of 1983, but after this date the model failed to simulate the observed seasonal cycle, which showed peaks during the northern autumn in 1983 and 1984.

Figure 39 depicts the evolutions of the simulated global volcanic temperature signals for about a half year before and about three and half years after the Mount Pinatubo eruptions, along with the observed signals (ERA-40). The model reproduced the observed warmings after the Mount Pinatubo eruption, such as the first warming in the 1991/92 winter, and the second and third warmings during autumn in 1992 and 1993, although it showed an extra weak warming during early summer in 1992. Quantitatively, however, the model overestimates the warming magnitude for the two eruptions, in particular for El Chichón, as have other model simulations (e.g., Dameris et al., 2005; Kirchner et al., 1999). One reason for this is the disagreement between the simulated and observed QBOs, because the QBO significantly influences the effect of volcanic aerosols (e.g., Randel et al., 1995) through the mean meridional circulation.

When El Chichón erupted, the ERA-40 QBO wind was easterly and had almost peaked at 50 hPa, above which a strong westerly shear was descending (Fig. 17). Similarly, the simulated QBO winds are approximately easterly maxima at 50 hPa (Fig. 18) for all members, whereas the maximum values (10 ms⁻¹) are about half the observed value (20 ms⁻¹). On the other hand, during the eruption of Mount Pinatubo, the observed QBO winds at 50 hPa were almost at the transition states from westerly to easterly and the westerly lasted abnormally long; that is, the descent of the next easterly stalled for several months at around 50 hPa (Fig. 17) after the eruption. The simulated QBO winds are near a peak value, and no abnormal feature can be seen regarding the descent of the next westerly after the eruption. Such differences in the QBO phase in relation to the eruptions between the observed and simulated data are in part responsible for the CCM errors, because the vertical shear of the QBO is directly related to the secondary meridional circulation, which produces large effects in up- and downdraft regions. In addition, these differences might produce the difference in the
response errors of the CCM between the two eruptions, although the spatial distribution of the volcanic aerosols is based on observations and has nothing to do with the QBO phase in the CCM.

The global (65°S to 65°N) volcanic total ozone signals for the El Chichón and Mount Pinatubo eruptions are depicted in Figs. 40 and 41. For the El Chichón eruption, the simulated ozone decrease peaked in February 1983, similar to the observed decrease. Other ozone decrease extremes in August 1982 and 1983, January 1984, and February 1985 were underestimated but their timings were correctly reproduced, although the simulated extrema in July 1984 cannot be seen in the observation data. For the Mount Pinatubo eruption, the simulation does not capture the observed features well, except for the temperature signal. The simulated ozone decrease firstly peaked in July 1992, about five months after the observed first extreme decrease in February 1992, and its magnitude is about three times the observed one. In addition, other observed ozone extremes, increase one centered in August 1992 and decrease one in January 1993, are not reproduced at all in the simulation. The overall overestimation of the simulated ozone decrease results primarily from an overestimation of ozone loss due to the heterogeneous reactions on the volcanic aerosol surface, because the gas-phase reactions could not produce such a severe ozone decrease. Furthermore, radiative and dynamic effects are also responsible for this overestimation (e.g., Tie et al., 1994; Kinnison et al., 1994). The radiative effect refers to the warming below the middle stratosphere due to the solar and terrestrial heating of volcanic aerosols, leading to increases in the reaction rates of odd-oxygen loss, and the dynamic effect refers to the enhanced upward transport of ozone-poor air, which is a dynamic response to the radiative heating. Both effects induce an ozone loss below the middle stratosphere in the tropics.
5. Discussion

The QBO in the equatorial stratosphere crucially affects the stratospheric dynamics in both the tropics and in mid- and high latitudes through the wave-mean flow interaction. For the westward QBO wind, the zero-wind line seems to work as a critical line (e.g., Andrews et al., 1987) for stationary planetary waves in the winter hemisphere, and stationary planetary waves are thereby apt to deflect poleward; this gives them a larger westward momentum deposition in high latitudes, resulting in a weaker polar vortex and warmer polar temperatures. For the eastward QBO wind, however, there is no critical line in the winter hemisphere, so stationary planetary waves are apt to deflect equatorward, inducing a stronger polar vortex and colder polar temperatures. This relationship between the QBO phase and the magnitude of the polar vortex in the Northern Hemisphere was first demonstrated by Holton and Tan (1980) from monthly data covering a 16-year period (1962-1977), but its statistical significance in their study was marginal owing to the small numbers of the QBO phase.

Recently, Naito and Yoden (2005) proved that the above relationship (Holton-Tan relation) holds true with high statistical significance (> 99%) in long-term daily NCEP/NCAR reanalysis data (Kalnay et al., 1996) covering 46 years (1958-2003), obtained the large-sample method. Pascoe et al. (2005) also obtained statistically significant results for the Holton-Tan relation from the ERA-40 data set for 1979 to 2001. The Holton-Tan relation can also be reproduced by three-dimensional mechanistic models (e.g., Holton and Austin, 1991; Hampson and Haynes, 2006) and by GCMs by imposing the observed QBO wind (Hamilton, 1998).

The simulated QBO has a smaller amplitude and a slightly shorter period than the observed QBO (Fig. 21). As a result, the mean meridional circulation associated with the QBO also differs with respect to period and intensity, giving rise to different influences on chemical constituents in the tropics. In addition, both the zonal wind field in the subtropical stratosphere and the phase relationship between the QBO and the seasonal cycle in the simulation differ from those in the observation data, causing different extratropical responses to the QBO. This result is because the phase alignment or the relationship between the QBO and the seasonal cycle plays an important role in the extratropical responses (e.g., Gray and Dunkerton, 1990; Hampson and Haynes, 2006).

The QBO also affects the responses to the 11-year solar cycle (e.g., Labitzke, 1987; Labitzke and van Loon, 1988) and volcanic aerosols (e.g., Randel et al., 1995; Lee and Smith, 2003), with the result that the simulated responses to these forcings may be skewed to a certain degree because of the differently reproduced QBO, requiring some caution in interpreting the model result. The response to volcanic aerosols due to volcanic eruptions in the tropics such as the El Chichón and Mount Pinatubo eruptions in particular requires the phase relationship with the QBO to be correct, because the large amounts of volcanic aerosols initially formed in the QBO domain are subject to dynamic heating or cooling associated with the mean meridional circulation, which depends on the QBO phase. For example, if the simulated QBO phase is westerly (that is, opposite to the observed easterly phase), then radiative heating due to volcanic aerosols and dynamical heating are both positive, leading to warming errors. With the correct QBO phase (easterly), the dynamics leads to cooling by a downdraft, resulting in the suppression of radiative heating.
The simulated trend is probably free from the effect of the QBO, because the simulated QBO wind does not exhibit a trend like the observed trend. However, the validity of the assumption used in the multiple linear regression analysis of ozone must be treated with care. Specifically, the annual mean ozone trend is linear everywhere over the entire period from 1980 to 2004. The observed ozone, however, has recently exhibited a turnaround in certain latitude and altitude ranges. Fioletov et al. (2002), for example, found that total ozone measured by ground-based stations and satellite (TOMS and TOMS/SBUV) showed no substantial decreasing trend from 1988 to 2000 in the northern mid-latitudes (35° to 60°N). Newchurch et al. (2003) demonstrated that SAGE I/II data combined with HALOE data provide evidence of a slowdown in stratospheric ozone losses since 1997. Hadjinicolaou et al. (2005) showed that the TOMS/SBUV total ozone level increased between 35° and 60°N after 1994, in contrast to the decreasing trend observed previously (1979 to 1993) and that this upward trend is reproduced by the CTM forced only by transport changes. Therefore, a piecewise-linear model (e.g., Reinsel et al., 2005), rather than a linear model, is preferable for accurate representation of the observed and simulated trends, in spite of the increase of parameters.
6. Summary

Ensemble simulation of the middle atmosphere over the past 25 years (from 1980 to 2004) was performed with the MRI-CCM by imposing observed natural and anthropogenic forcings of SST, sea ice, greenhouse gases, halogens, the 11-year solar cycle, and volcanic aerosols. These forcings were imposed daily by interpolation of monthly mean values. The monthly mean SSTs were corrected to retain temporal variability even when interpolated from monthly to daily values. The concentrations of well-mixed GHGs (CO₂, CH₄, and N₂O) and those of halogens are specified at the surface. In addition, the abundance of each chlorine-bearing species is multiplied by a nearly constant factor (1.3) each month to realistically represent the abundance of total chlorine atoms (CClᵧ) in organic chlorine compounds.

MRI-CCM adopts a hybrid semi-Lagrangian transport scheme, which is an ordinary semi-Lagrangian scheme in the horizontal direction and takes a form equivalent to a mass-conserving flux in the vertical direction. The current PRM5 scheme, which uses quintic interpolation in the horizontal direction and employs a piecewise rational method for determination of overhead column abundances in the vertical direction, produced a substantial decrease in positive ozone biases, particularly in the tropical upper troposphere and lower stratosphere, compared with the previous scheme that used cubic interpolation for both the horizontal and vertical directions. As a side effect of the decrease in ozone in the tropical lower stratosphere, the QBO period shortened from 31 to 20 months as a result of the decrease in the solar-heating feedback of ozone. To prolong the QBO period to a realistic value, the horizontal diffusion is weakened (that is, the e-folding time of the horizontal diffusion is decreased to about a half in the middle atmosphere), resulting in a QBO period of 27 months. The other features of the QBO are very similar to those of the previous model, with a 31-month period simulated under annually repeating forcings.

Multiple linear regression analysis was performed for temperature, zonal wind, and ozone to separate the trend, the QBO, the El Chichón and Mount Pinatubo, the 11-year solar cycle, and the ENSO signals for the simulation and observation data. It was found that the MRI-CCM can more or less realistically reproduce the observed trend of annual mean temperature and ozone such as the maximum cooling of 2 K/decade near the tropical and subtropical stratopause and the maximum ozone decrease of 12%/decade at 2 to 3 hPa altitude around 30° to 60° latitude in both hemispheres. Total ozone exhibits severe spring-time decreases of 3%/decade in the northern high latitudes and of 7%/decade in the southern high latitudes, which are respectively 1%/decade higher and 3%/decade higher than the observed values. The annual mean QBO signals of temperature and zonal wind are well reproduced with regard to their meridional structures, which are characterized by two or three cells with alternating signs in the stratosphere, in spite of the slightly shorter QBO period of 27 months. Similarly, the simulated ozone QBO signal also captures the observed meridional structure of vertical multi-cells. The seasonality of the mid-latitude total ozone QBO, which extends poleward with opposite sign to the equatorial total ozone QBO in the winter hemisphere, is also quantitatively reproduced in the QBO20 signal, although there is no extension to high latitudes in the spring time.

The simulated annual mean temperature signal related to the 11-year solar cycle shows two strong warming altitudes: in the upper stratosphere near the stratopause
and in the lower stratosphere centered at about 70 hPa. The upper stratospheric warming has two peaks of about 0.8 K at 30° in both hemispheres and occupies a wide latitudinal belt from 60°S to 60°N, with further extension to both polar regions. The lower stratospheric warming has a peak at 70 hPa extending from 30°S to 30°N. As a result of these two strong warming altitudes, there appears a minimum warming altitude at around 5 hPa. Also, in the simulated annual mean ozone signal shows two maxima in the tropics/subtropics: one is in the upper stratosphere at 3 hPa with a peak of about 2.8% and the other is in the lower stratosphere at around 70 hPa with a peak of 3.6%. These simulated temperature and ozone patterns are similar to the observed annual mean solar signals.

The annual average ENSO signal in zonal mean temperature in the tropics is well reproduced in terms of the spatial pattern of tropospheric warming and the stratospheric cooling, although the amplitudes are underestimated by about half. The simulated mid-latitude stratospheric warming in both hemispheres is slightly higher than the observed values. The ENSO signal of zonal-mean zonal wind, represented as the subtropical jet intensification on the equatorward flank in both hemispheres, is also well captured. The stratospheric ENSO ozone signal, which manifests as an ozone decrease in the tropics and an ozone increase in the mid-latitudes centered at about 35°S to 35°N, though slightly overestimated, is well reproduced.

The global (65°S to 65°N) volcanic temperature increase signals due to the El Chichón and Mount Pinatubo eruptions are twice as large as the observed signals, but the seasonal variations are approximately the same because the spatial distribution and radiative properties of the volcanic aerosols are based on observed values. However, the global volcanic ozone decrease signals are overestimated, in particular for Mount Pinatubo, though the observed surface-area densities of the volcanic aerosols are imposed.

Acknowledgments

This study was supported by the Global Environmental Research Fund (GERF) of the Ministry of the Environment (MOE) of Japan. The ensemble simulation was calculated on the supercomputers at the National Institute for the Environmental Studies, and that in the Meteorological Research Institute, Japan.
References


References


References


References


Appendix I: Formulation of Transport

I-1 Mass Transport

The continuity equation for the $\eta$-ordinate is expressed by

$$\frac{\partial}{\partial t} \left( \frac{\partial p}{\partial \eta} \right) + \nabla \left( \mathbf{v} \frac{\partial p}{\partial \eta} \right) + \frac{\partial}{\partial \eta} \left( \dot{\eta} \frac{\partial p}{\partial \eta} \right) = 0,$$

(I.1)

where $p$ is the pressure and $\mathbf{v}$ is the horizontal wind. Differentiation of the second term on the left-hand side by parts leads to

$$\frac{\partial}{\partial t} \left( \frac{\partial p}{\partial \eta} \right) + \mathbf{v} \cdot \nabla \frac{\partial p}{\partial \eta} = -\left( \nabla \cdot \mathbf{v} \right) \frac{\partial p}{\partial \eta} - \frac{\partial}{\partial \eta} \left( \dot{\eta} \frac{\partial p}{\partial \eta} \right).$$

(I.2)

Multiplication of Eq.(I.2) by an operator $\int_{k-1/2}^{k+1/2} d\eta$ and use of the following relation,

$$\int_{k-1/2}^{k+1/2} \frac{\partial p}{\partial \eta} d\eta = p_k^{k+1/2} - p_k^{-1/2} = -\triangle p_k$$

produce

$$\frac{\partial}{\partial t} \triangle p_k + \mathbf{v}_k \cdot \nabla \triangle p_k = -\left( \nabla \cdot \mathbf{v} \right)_k \triangle p_k + \left( \dot{\eta} \frac{\partial p}{\partial \eta} \right)_{k+1/2} - \left( \dot{\eta} \frac{\partial p}{\partial \eta} \right)_{k-1/2},$$

(I.3)

where the subscripts $+1/2$ and $-1/2$ represent the half-levels. Since the sum of the temporal and spatial derivatives on the left-hand side of Eq.(I.3) represents the total derivative due to the horizontal advection, we denote this as $\frac{D_h}{Dt}$. Then,

$$\frac{D_h}{Dt} \triangle p_k = -\left( \nabla \cdot \mathbf{v} \right)_k \triangle p_k + \left[ \left( \dot{\eta} \frac{\partial p}{\partial \eta} \right)_{k+1/2} - \left( \dot{\eta} \frac{\partial p}{\partial \eta} \right)_{k-1/2} \right].$$

(I.4)

This is the governing equation, which so far contains no approximation. Next, on the basis of physical concept, we modify Eq.(I.4) to a desired form for the numerical transport of mass.

Henceforth, a leapfrog scheme of three-time level is used for the time derivative and the values at $t + \triangle t$, $t$, and $t - \triangle t$ are denoted with the superscripts $+, 0$, and $-$, respectively. Further, we use superscripts $A$ and $D$ for the values at the departure and arrival points resulting from the horizontal advection. Then, an approximation of all terms on the right hand side of Eq.(I.4) with the arithmetic mean of the values at the departure and arrival points yields

$$\frac{\triangle p_k^A - \triangle p_k^D}{2\triangle t} =$$

$$-\frac{1}{2} \left[ \left( \nabla \cdot \mathbf{v} \right)_k^{+D0} \triangle p_k^{+D0} + \left( \nabla \cdot \mathbf{v} \right)_k^{-A0} \triangle p_k^{-A0} \right] + \frac{1}{2} \left[ \left( \dot{\eta} \frac{\partial p}{\partial \eta} \right)^{A0} \right]_{k+1/2} - \left( \dot{\eta} \frac{\partial p}{\partial \eta} \right)^{A0} \right]_{k-1/2} + \left( \dot{\eta} \frac{\partial p}{\partial \eta} \right)^{D0} \right]_{k+1/2} - \left( \dot{\eta} \frac{\partial p}{\partial \eta} \right)^{D0} \right]_{k-1/2},$$

(I.5)
where the superscript * means that the variable has only physical meaning without definite form, which will be determined afterward. Arranging Eq. (I.5) so that the arrival and departure variables appear only on the left- and right-hand sides, respectively, gives

\[
\Delta p_k^{A+} - \Delta t \left[ \left( \eta \frac{\partial p}{\partial \eta} \right)_{k+1/2}^{A} - \left( \eta \frac{\partial p}{\partial \eta} \right)_{k-1/2}^{A} \right] + \Delta t (\nabla \cdot \mathbf{v})_k^{*A0} \Delta p_k^{*A} = \Delta p_k^{D-} + \Delta t \left[ \left( \eta \frac{\partial p}{\partial \eta} \right)_{k+1/2}^{D0} - \left( \eta \frac{\partial p}{\partial \eta} \right)_{k-1/2}^{D0} \right] - \Delta t (\nabla \cdot \mathbf{v})_k^{*D0} \Delta p_k^{*D}. \tag{I.6}
\]

Here, the following two pressure increments are defined:

\[
\Delta \tilde{p}_k^{A+} \equiv \Delta p_k^{A+} - \Delta t \left[ \left( \eta \frac{\partial p}{\partial \eta} \right)_{k+1/2}^{0} - \left( \eta \frac{\partial p}{\partial \eta} \right)_{k-1/2}^{0} \right], \tag{I.7a}
\]

\[
\Delta \tilde{p}_k^{D-} \equiv \Delta p_k^{D-} + \Delta t \left[ \left( \eta \frac{\partial p}{\partial \eta} \right)_{k+1/2}^{D0} - \left( \eta \frac{\partial p}{\partial \eta} \right)_{k-1/2}^{D0} \right]. \tag{I.7b}
\]

Eq. (I.7) defines the values at the arrival points (i.e., the grid points) and the departure points, and it can be interpreted, by removing the superscript A and D, as the definitions of \( \tilde{p}^+ \) and \( \tilde{p}^- \) at the grid points:

\[
\Delta \tilde{p}_k^{+} \equiv \Delta p_k^{+} - \Delta t \left[ \left( \eta \frac{\partial p}{\partial \eta} \right)_{k+1/2}^{0} - \left( \eta \frac{\partial p}{\partial \eta} \right)_{k-1/2}^{0} \right], \tag{I.7c}
\]

\[
\Delta \tilde{p}_k^{-} \equiv \Delta p_k^{-} + \Delta t \left[ \left( \eta \frac{\partial p}{\partial \eta} \right)_{k+1/2}^{0} - \left( \eta \frac{\partial p}{\partial \eta} \right)_{k-1/2}^{0} \right]. \tag{I.7d}
\]

Eq. (I.7) implies that time integration in the vertical is equal to the transformation of the pressure ordinate from \( \Delta p_k \) to \( \Delta \tilde{p}_k \) and \( \Delta \tilde{p}_k \), or equivalently from \( p \) to \( \tilde{p} \) and \( \tilde{p} \). Note that the sign of the second term on the right-hand side of Eqs. (I.7a, c) is opposite to that of Eqs. (I.7b, d). This indicates that the time integration should go backward and forward with a half of the total time step to obtain \( \Delta \tilde{p}_k^{+} \) at the arrival point and \( \Delta \tilde{p}_k^{-} \) at the departure point.

The forms of the variables with superscript * in Eq. (I.5) are then described by the following approximation by using velocities \( \mathbf{v} \) in the \( \tilde{p}^+ \) ordinate and \( \tilde{\mathbf{v}} \) in the \( \tilde{p}^- \) ordinate:

\[
(\nabla \cdot \mathbf{v})_k^{*A0} \Delta p_k^{*A+} \to (\nabla \cdot \mathbf{v})_k^{A0} \Delta \tilde{p}_k^{A+}, \tag{I.8a}
\]

\[
(\nabla \cdot \mathbf{v})_k^{*D0} \Delta p_k^{*D-} \to (\nabla \cdot \tilde{\mathbf{v}})_k^{D0} \Delta \tilde{p}_k^{D-}, \tag{I.8b}
\]

where \( \nabla \mathbf{v}_k \) and \( (\nabla \cdot \mathbf{v})_k^{A0} \) and \( (\nabla \cdot \tilde{\mathbf{v}})_k^{D0} \) represent the divergence at \( t = t \) in the pressure ordinate \( \tilde{p}_k^{A+} \) and \( \tilde{p}_k^{D-} \), respectively. Eqs. (I.6)-(I.8) finally lead to

\[
\Delta \tilde{p}_k^{A+} + \Delta t (\nabla \cdot \mathbf{v})_k^{A0} \Delta \tilde{p}_k^{A+} = \Delta \tilde{p}_k^{D-} - \Delta t (\nabla \cdot \tilde{\mathbf{v}})_k^{D0} \Delta \tilde{p}_k^{D-},
\]
or equivalently,
\[
\Delta p_k^{A+} \left( 1 + \Delta t (\nabla \cdot v)_k^0 \right)^A = \Delta \tilde{p}_k^{D-} \left( 1 - \Delta t (\nabla \cdot \tilde{v})_k^0 \right)^D
\]
\[
= \left[ \Delta \tilde{p}_k^{-} \left( 1 - \Delta t (\nabla \cdot \tilde{v})_k^0 \right) \right]^D. \tag{I.9a}
\]
Thus,
\[
\Delta p_k^{A+} = \left[ \Delta \tilde{p}_k^{-} \left( 1 - \Delta t (\nabla \cdot \tilde{v})_k^0 \right) \right]^D / \left( 1 + \Delta t (\nabla \cdot \tilde{v})_k^0 \right)^A. \tag{I.9b}
\]

A schematic comparison between the ordinary semi-Lagrange transport scheme and
the hybrid semi-Lagrange transport scheme is drawn in Fig.(I-1). The ordinary semi-
Lagrange transport scheme is simply to search the departure in three dimensional space
using horizontal velocity \((u, v)\) and vertical velocity \((w)\). On the other hand, in the
hybrid semi-Lagrange transport scheme, the vertical transport is separately evaluated
as displacements during a half time step at departure and arrival, leading to the working
pressure ordinates, \(\tilde{p}^{-}\) at departure and \(\tilde{p}^{+}\) at arrival, on the surface of which the
departure is searched.

The mass field, that is, pressure field \(p^{+}\) at \(t = t + \Delta t\) can be calculated by using
Eq.(I.9) when the surface pressure \(P_s^{-}\) at \(t = t - \Delta t\), and \(P_s^0\), \((\eta \frac{\partial p}{\partial \eta})^0\), \(v^0\), and
\((\nabla \cdot v)^0\) at \(t = t\) are given. The procedure to calculate \(p^{A+}\) is as follows. By vertically
integrating Eq.(I.7a) from the top layer \((k=k_{\text{max}})\) to the lowest layer \((k=1)\) using \(\dot{\eta} = 0\)
at \(k=1\) and \(k=k_{\text{max}}\), we get
\[
P_s^{A+} = \sum_{k_{\text{max}}}^{1} \Delta p_k^{A+} = \sum_{k_{\text{max}}}^{1} \Delta \tilde{p}_k^{A+}. \tag{I.10}
\]
On the other hand, pressure is expressed in the \(\eta\)-ordinate by
\[
p(x, y, z, t) = A(z) + B(z) \cdot P_s(x, y, t), \tag{I.11}
\]
where \(A(z)\) and \(B(z)\) are constants depending only on height. Though Eqs.(I.9)-(I.11)
formally give \(p^{A+}\), Eq.(I.9) implicitly includes \(p^{A+}\) through \(\tilde{v}\), indicating that some
iterative calculation is required to solve Eqs.(I.9)-(I.11). We use the following iterative
method.

\((i_1)\) Calculate \(p^{-}\) using the relation \(\Delta p_k^{-} = \Delta A_k + \Delta B_k \cdot P_s(t - \Delta t)\), and obtain \(\Delta \tilde{p}^{-}\)
and \(\tilde{p}^{-}\) from Eq.(I.7d).

\((i_2)\) Calculate the coefficients of the cubic Lagrange interpolation from \(p^{-}\) to \(\tilde{p}^{-}\) ordinate.

\((i_3)\) Interpolate \(\tilde{v}^0\) and \((\nabla \cdot \tilde{v})^0\) from \(v^0\) and \((\nabla \cdot v)^0\) by using the coefficient obtained
above.

\((i_4)\) Calculate \(\Delta \tilde{p}_k^{-} \left( 1 - \Delta t (\nabla \cdot \tilde{v})_k^0 \right)\).
Appendix I: Formulation of Transport

(i5) Calculate $\Delta p^+$ using $P^+_s$ as a first guess of $P^+_s$: $\Delta p^+_k = \Delta A_k + \Delta B_k \cdot P^+_s$, and obtain $\Delta \bar{p}^+$ and $\bar{p}^+$ from Eq.(I.7c).

(i6) Calculate the coefficients of the cubic Lagrange interpolation from $p^+$ to $\bar{p}^+$ ordinates.

(i7) Interpolate $\nabla^0$ and $(\nabla \cdot \nabla)^0$ from $\nabla^0$ and $(\nabla \cdot \nabla)^0$ using the coefficient obtained in (i6).

(i8) Calculate the departure point location using $\nabla^0$ as the arrival point wind and $\bar{\nabla}^0$ as the departure point wind with a cubic Lagrange interpolation. Note that the time step is $2\Delta t$.

(i9) Interpolate the departure point value $[\Delta \bar{p}_k^-(1 - \Delta t(\nabla \cdot \bar{\nabla})^0_k)]^D$ from the grid point value $\Delta \bar{p}_k^-(1 - \Delta t(\nabla \cdot \bar{\nabla})^0_k)$.

(i10) Evaluate $\Delta \bar{p}_k^+$ from Eq.(I.9b).

(i11) Obtain $P^+_s$ from (I.10).

(i12) Update $p^+$ and $\bar{p}^+$, and repeat the (i6) to (i11) loop.

With regard to mass conservation, the vertical transport conserves mass while the horizontal transport does not, because the former is expressed by the transformations of pressure ordinates, Eqs.(I.7a,b), which conserve the surface pressure as seen in Eq.(I.10). Some correction for mass is thus required owing to the horizontal transport. We use the method proposed by Gravel and Staniforth(1994), in which the high-order interpolation is set to cubic as stated in (i4) and the low-order interpolation is set to linear. This method decreases (increases) the mass by multiplying by a constant factor only the points where the high-order interpolated mass is greater (smaller) than the low-order interpolated mass, if the global mass change due to transport is positive (negative).

In general, $P^+_s$ calculated by this method in the chemistry module does not necessarily coincide with that calculated in the dynamical module. Rather, there is always a difference between them. Since the latter is consistent with other dynamics variables, it should be reflected in the $P^+_s$. Thus, the relation $\Delta p_k = \Delta A_k + \Delta B_k \cdot P^+_s$ leads to the following modification for maintaining consistency between the transport-determined surface pressure $P^+_s$ and the dynamics-determined surface pressure $P^+_s$:

$$\Delta p_k^+ = \Delta p_k^+ + \Delta B_k(P^+_s - P^+_s)$$

(I.12)

where $\Delta p_k^+$ on the right-hand side is the output of the iteration loop (i6)-(i11).

I-2 Species Transport

For a chemical species with volume mixing ratio $q$ the transport equation is expressed by

$$\frac{\partial}{\partial t} q + \nabla q + D \frac{\partial}{\partial t} q = 0.$$  

(I.13)

We convert this into a flux-form with the use of Eq.(I.1)

$$\frac{\partial}{\partial t} \left( \frac{\partial p}{\partial \eta} \right) + \nabla \left( \nabla \frac{\partial p}{\partial \eta} q \right) + \frac{\partial}{\partial \eta} \left( \eta \frac{\partial p}{\partial \eta} q \right) = 0.$$  

(I.14)
Eq. (I.14) becomes the same as Eq. (I.1) by replacing $\delta p \cdot q$ with $\delta p$. Thus by following a similar procedure as in the mass transport, we get an equation similar to Eq. (I.9a)

$$(\nabla \mathbf{p}_k \cdot \nabla q)^{A+} \left(1 + \Delta t(\nabla \mathbf{v})_k^0\right)^A = (\nabla \mathbf{p}_k \cdot \nabla q)^{D-} \left(1 - \Delta t(\nabla \mathbf{v})_k^0\right)^D,$$  \hspace{1cm} (I.15)

where $\nabla q^{A+}$ and $\nabla q^{D-}$ represent the value of $q_k^{A+}$ before the vertical transport and the value of $q_k^{D-}$ after the vertical transport, respectively, and they are defined as

$$(\nabla \mathbf{p}_k \cdot \nabla q)^{A+} = (\nabla \mathbf{p}_k \cdot \nabla q)^{A+} - \Delta t \left[ \left( \eta \frac{\partial p}{\partial \eta} q \right)^{A0}_{k+1/2} - \left( \eta \frac{\partial p}{\partial \eta} q \right)^{A0}_{k-1/2} \right],$$  \hspace{1cm} (I.16a)

$$(\nabla \mathbf{p}_k \cdot \nabla q)^{D-} = (\nabla \mathbf{p}_k \cdot \nabla q)^{D-} + \Delta t \left[ \left( \eta \frac{\partial p}{\partial \eta} q \right)^{D0}_{k+1/2} - \left( \eta \frac{\partial p}{\partial \eta} q \right)^{D0}_{k-1/2} \right].$$  \hspace{1cm} (I.16b)

It should be pointed out that Eqs. (I.16a, b) are evaluated not directly but by physical evaluation to obtain $\nabla q^{A+}$ and $\nabla q^{D-}$. For example, $\nabla q_{k-}$ represents the cell(grid)-averaged value in $\nabla q_{k-}$ (right panel in Fig.I-2) after the vertical transport from the half-level above and from the half-level below (left panel in Fig.I-1). So that, once the transformation of vertical spacing from $\Delta p_k^{-}$ to $\Delta \nabla q_{k-}$ is made (middle panel in Fig.I-2), then $\nabla q_k$ can be calculated by integrating $q(p)^{-}$ in $\Delta \nabla q_{k-}$ (right panel in Fig.I-2). To reduce the computation time, we use the following simple method to calculate $\nabla q_k$.

Consider the following column function of mixing ratio $q^-$ accumulated downward from the top,

$$F(p^-) = \int_{p_{top}}^{p^-} q^- dp^-,$$  \hspace{1cm} i.e.,

$$F(p_{kmax+1/2}^-) = 0,$$

$$F(p_{kmax-1/2}^-) = (\nabla p_{kmax} \cdot q_{kmax})^-,$$

$$F(p_{kmax-3/2}^-) = F(p_{kmax-1/2}^-) + (\nabla p_{kmax-1} \cdot q_{kmax-1})^-,$$

$$\ldots$$

$$F(p_{kmax-j+1/2}^-) = F(p_{kmax-j+1/2}^-) + (\nabla p_{kmax-j} \cdot q_{kmax-j})^-,$$

$$\ldots$$  \hspace{1cm} (I.17)

Note that $F(p^-)$ is a monotonically increasing function of $p$, and its in-cell profile can be thereby represented the more accurately by the piecewise rational method (PRM), which conserves the cell average, as will be described in detail later.

Next, calculate the column function at each half-level of the working pressure ordinate $\nabla p_k^-$ by the PRM, which piecewise requires in-cell profiles of $q^-$ as functions of $p^-$. In other words, obtain $F(\nabla p_{kmax-1/2}^-), \ldots, F(\nabla p_{k+1/2}^-), \ldots, F(\nabla p_{3/2}^-), F(\nabla p_{1/2}^-)$. The boundary conditions at the top and bottom impose mass-conservation constraints:

$$F(p_{kmax+1/2}^-) = F(\nabla p_{kmax+1/2}^-) = 0,$$

$$F(p_{1/2}^-) = F(\nabla p_{1/2}^-).$$  \hspace{1cm} (I.18)
Then, the cell average volume mixing ratio can be calculated as

\[
\bar{q}_{k_{\text{max}}} = \frac{F(p_{k_{\text{max}}-1/2}^-) - F(p_{k_{\text{max}}+1/2}^-)}{\Delta p_{k_{\text{max}}}},
\]

\[
\bar{q}_{k_{\text{max}}-1} = \frac{F(p_{k_{\text{max}}-3/2}^-) - F(p_{k_{\text{max}}-1/2}^-)}{\Delta p_{k_{\text{max}}-1}},
\]

\[
\bar{q}_{k_{\text{max}}-j} = \frac{F(p_{k_{\text{max}}-j-1/2}^-) - F(p_{k_{\text{max}}-j+1/2}^-)}{\Delta p_{k_{\text{max}}-1}}, \quad j=0,1,\ldots
\]

\[\tag{I.19}\]

Since the departure point is already known in the mass transport routine, the volume mixing ratio at the departure point, \(\bar{q}^D^-\), is calculated from \(\bar{q}^-\) by quintic Lagrangian interpolation. Then, from Eqs.(I.9) and (I.15) we get

\[\bar{q}^{A+} = \bar{q}^D-.\] \[\tag{I.20}\]

Since the quintic Lagrangian interpolation corresponds to the high-order interpolation, the low-order interpolation uses cubic Lagrangian interpolation, with regard to the conservation of species mass in the horizontal transport (cf. cubic and linear for the air mass). Finally, the desired quantity \(\bar{q}^{A+}\) can be obtained from \(\bar{q}^{A+}\) by transformation of the pressure ordinate from \(p_k^+\) to \(p_k^-\), following a similar procedure to that in Eqs.(I.17)-(I.19).

I-3 Interpolating Interface Values

Reconstruction of an in-cell profile needs not only cell averages but also cell interfaces with neighboring cells. Let \(\bar{f}_i\) be the cell average in \(i\)-th cell and its left and right interface grids be \(x_{i-1/2}\) and \(x_{i+1/2}\). The in-cell profile \(f(x)\) to be determined has a constraint conserving the cell average:

\[
\bar{f}_i = \frac{1}{\Delta x_i} \int_{x_{i-1/2}}^{x_{i+1/2}} f(x) dx, \tag{I.21a}\]

\[
\Delta x_i = x_{i+1/2} - x_{i-1/2}. \tag{I.21b}\]

Since the in-cell profile of the \(i\)-th cell is not necessarily continuous at interfaces with those of neighboring (i-1)-th and (i+1)-th cells, values at these two interfaces are referred to as \(\bar{f}_i^L\) and \(\bar{f}_i^R\).

First, we calculate the cell interface from the cell averages with a cubic polynomial. Consider a configuration of four sequentially aligned cells shown in Fig.I-3. The constraint of the cubic polynomial is that it has the same cell averages as the four cells surrounding the cell interface located at \(x_{i-1/2}\), namely \(\bar{f}_{i-2}\), \(\bar{f}_{i-1}\), \(\bar{f}_i\) and \(\bar{f}_{i+1}\). Consider the integral of the cubic polynomial \(f(x)\) starting from \(x_{i-5/2}\):

\[y(x) = \int_{x_{i-5/2}}^{x} f(x) dx. \tag{I.22}\]

Thus, \(y(x)\) becomes a quartic polynomial with the constraint:

\[
y(x_{i-5/2}) = 0
\]

\[
y(x_{i-3/2}) = \bar{f}_{i-2} \Delta x_{i-2},
\]

\[
y(x_{i-1/2}) = \bar{f}_{i-2} \Delta x_{i-2} + \bar{f}_{i-1} \Delta x_{i-1}, \tag{I.23}
\]

\[
y(x_{i+1/2}) = \bar{f}_{i-2} \Delta x_{i-2} + \bar{f}_{i-1} \Delta x_{i-1} + \bar{f}_i \Delta x_i,
\]

\[
y(x_{i+3/2}) = \bar{f}_{i-2} \Delta x_{i-2} + \bar{f}_{i-1} \Delta x_{i-1} + \bar{f}_i \Delta x_i + \bar{f}_{i+1} \Delta x_{i+1}.
\]
For simplicity, we use the following notations:

\[ [x_1, x_2, x_3, x_4, x_5] = [x_{i-5/2}, x_{i-3/2}, x_{i-1/2}, x_{i+1/2}, x_{i+3/2}], \quad (I.24a) \]

\[ [y_1, y_2, y_3, y_4, y_5] = [y(x_{i-5/2}), y(x_{i-3/2}), y(x_{i-1/2}), y(x_{i+1/2}), y(x_{i+3/2})] \]

Then, from the definition Eq.(I.22) of \( y(x) \) the cell interface at \( x_3 = x_{i-1/2} \) is given as the derivative of the quartic function:

\[
y(x) = y_1 + \left( x - x_1 \right) \left\{ [x_2, x_1] + \left( x - x_2 \right) [x_3, x_2, x_1] + \left( x - x_3 \right) [x_4, x_3, x_2, x_1] + \left( x - x_4 \right) [x_5, x_4, x_3, x_2, x_1] \right\}, \quad (I.25)\]

where the brackets \([\quad]\) represent divided differences:

\[
[x_1, x_2] = [x_2, x_1] = \frac{y_2 - y_1}{x_2 - x_1}, \quad (I.26a)\]

and

\[
[x_1, x_2, \cdots, x_n] = \frac{[x_1, x_2, \cdots, x_{n-2}, x_{n-1}] - [x_1, x_2, \cdots, x_{n-2}, x_n]}{x_{n-1} - x_n}. \quad (I.26b)\]

Then, from the definition Eq.(I.22) of \( y(x) \) the cell interface at \( x_3 = x_{i-1/2} \) is given as the derivative of the quartic function:

\[
f^L_{i} = f_{i-1/2} = (d/dx) y(x_3)
= [x_2, x_1] + (2x_3 - x_2 - x_1) [x_3, x_2, x_1]
+ (x_3 - x_1) (x_3 - x_2) [x_4, x_3, x_2, x_1]
+ (x_3 - x_1) (x_3 - x_2) (x_3 - x_4) [x_5, x_4, x_3, x_2, x_1]. \quad (I.27)\]

Manipulation of Eqs.(I.24)-(I.27) leads to

\[
f_{i-1/2} = \tilde{f}_{i-1} + \frac{\Delta x_{i-1}}{\Delta x_{i-1} + \Delta x_i} (\tilde{f}_i - \tilde{f}_{i-1}) + \frac{1}{\sum_{k=-2}^{1} \Delta x_{i+k}} \times \left\{ \frac{2\Delta x_i \Delta x_{i-1}}{\Delta x_{i-1} + \Delta x_i} \left[ \frac{\Delta x_{i-2} + \Delta x_{i-1}}{2\Delta x_{i-1} + \Delta x_i} - \frac{\Delta x_{i+1} + \Delta x_i}{2\Delta x_i + \Delta x_{i-1}} \right] \right\} (\tilde{f}_i - \tilde{f}_{i-1})
- \Delta x_{i-1} \frac{\Delta x_{i-2} + \Delta x_{i-1}}{2\Delta x_{i-1} + \Delta x_i} \delta \tilde{f}_i + \Delta x_i \frac{\Delta x_i + \Delta x_{i+1}}{\Delta x_{i-1} + 2\Delta x_i} \delta \tilde{f}_{i-1}, \quad (I.28)\]
where $\delta f_i$ is the i-th cell average slope of the parabolic in-cell profile interpolation described below:

$$
\delta f_i = \frac{\Delta x_i}{\Delta x_{i-1} + \Delta x_i + \Delta x_{i+1}} \left\{ \frac{2\Delta x_i + \Delta x_{i+1}}{\Delta x_i + \Delta x_{i+1}} (f_{i+1} - f_i) - \frac{2\Delta x_{i+1} + \Delta x_i}{\Delta x_i + \Delta x_{i-1}} (f_i - f_{i-1}) \right\},
$$

(I.29)

and likewise for $\delta f_{i+1}$.

Consider three sequential cells, similar to Fig.I-3, and obtain a parabolic interpolation function conserving these three cell averages $\bar{f}_{i-1}$, $\bar{f}_i$, and $\bar{f}_{i+1}$ for the three cells,

$$
f(x) = \alpha + \beta x + \gamma x^2.
$$

(I.30)

Then, the average slope is represented by $\beta$, because

$$
\int_{x_1}^{x_2} \left( \frac{d}{dx} f(x) \right) dx / \int_{x_1}^{x_2} dx = \beta.
$$

(I.31)

Following a procedure similar to the four-cell interpolation, the three coefficients in the parabola Eq.(I.30) can be calculated by using Newton’s interpolation. For $y(x) = \int f(x)dx$, the cubic polynomial $y(x)$ is represented as

$$
y(x) = y_1 + (x - x_1) \left\{ [x_2, x_1] + (x - x_2) [x_3, x_2, x_1] + (x - x_3) [x_4, x_3, x_2, x_1] \right\}.
$$

(I.32)

Since $\beta/2$ corresponds to the coefficient of the quadratic term in $y(x)$,

$$
\delta \bar{f}/2 = \beta/2 = [x_3, x_2, x_1] + (x_1 + x_2 + x_3) [x_4, x_3, x_2, x_1]
$$

(I.33)

By setting the middle point of $x_2$ and $x_3$ at the origin, the four cell interfaces become

$$
x_1 = -1/2 \Delta x_i - \Delta x_{i-1},
$$

$$
x_2 = -1/2 \Delta x_i,
$$

$$
x_3 = 1/2 \Delta x_i,
$$

$$
x_4 = 1/2 \Delta x_i + \Delta x_{i+1}.
$$

(I.34)

Inserting Eqs.(I.33) and (I.34) into Eq.(I.32) and rearranging the resultant equation leads to the functional form for the average slope of Eq.(I.29).
I-4 Piecewise Rational Method (PRM)

Consider the following derivative:

\[
\frac{d}{d\xi} \left( \frac{a\xi + b\xi^2}{1 + \beta\xi} \right) = \frac{a + 2b\xi + \beta b\xi^2}{(1 + \beta\xi)^2}, \quad (\beta \neq -1).
\]  

(I.35)

Then, by defining the rational function on the right-hand side of Eq.(I.34) as \( R(\xi) \), that is,

\[
R(\xi) \equiv \frac{a + 2b\xi + \beta b\xi^2}{(1 + \beta\xi)^2},
\]  

(I.36)

\( R(\xi) \) becomes an analytically integrable function

\[
\int_{\xi_i}^{\xi_f} R(\xi) \, d\xi = \int_{\xi_i}^{\xi_f} \frac{a\xi + b\xi^2}{1 + \beta\xi} \, d\xi = \frac{a\xi_i + b\xi_i^2}{1 + \beta\xi_i},
\]  

(I.37)

where \( \xi_i \) is a normalized coordinate defined by

\[
\xi_i = \frac{x - x_{i-1/2}}{x_{i+1/2} - x_{i-1/2}}, \quad (x_{i-1/2} \leq x \leq x_{i+1/2}).
\]  

(I.38)

Eqs. (I.36)-(I.38) mean that when an in-cell profile is represented by \( R(\xi) \), then the integral from its interface to an arbitrary point within the cell can be evaluated exactly.

When cell average \( \bar{f}_i \), and cell interfaces \( f_{i-1/2} \) and \( f_{i+1/2} \) are specified, that is,

\[
R_i(0) = f_{i-1/2}, \\
R_i(1) = f_{i+1/2}
\]

(I.39)

\[
\int_0^1 R_i(\xi) \, d\xi = \bar{f}_i
\]

all the coefficients in PRM can be readily determined:

\[
a = f_{i-1/2}, \\
b = \beta \bar{f}_i + f_{i-1/2} \\
\beta = \frac{f_{i-1/2} - f_i}{f_i - f_{i+1/2} + \epsilon} - 1
\]

(I.40)

where \( \epsilon \) is a small positive to avoid division by zero when \( f_i - f_{i+1/2} = 0 \).

Thus the integral of \( R(\xi) \) (I.37) can be expressed as

\[
\int_0^\xi R_i(\xi) \, d\xi = -\frac{g_i \xi \cdot h_i (1 - \xi)}{g_i \xi + h_i (1 - \xi) + \text{sign}(\epsilon, g_i + h_i)} + \bar{f}_i \xi
\]

(I.41a)

where

\[
g_i = \bar{f}_i - f_{i-1/2}, \\
h_i = f_{i+1/2} - \bar{f}_i
\]

(I.41b)

\[
\text{sign}(\epsilon, \alpha) = \begin{cases} 
\epsilon, & \text{for } \alpha \geq 0 \\
-\epsilon, & \text{for } \alpha < 0
\end{cases}
\]
Appendix I: Formulation of Transport

So far the $x$-coordinate is numbered in increasing order, that is, $x_i < x_{i+1}$, whereas the layer (level) of the pressure in the MRI-CCM is numbered in decreasing order, that is, $p_{k_{\text{max}}} < \ldots < p_{k+1} < p_k < p_{k-1} \ldots < p_1$, where $k_{\text{max}}$ is the number of layers. Hence, some modification is required for the MRI-CCM pressure ordinate. Yet, interface values (I.28) and average slope (I.29) are unchanged if the pressure increment is maintained as positive, that is, $\Delta p_i \equiv p_{i-1/2} - p_{i+1/2} > 0$.

The integral of $R(\xi)$ from the top of i-th cell is the same as (I.41a,b) except for

\[
\xi = \frac{p - p_{i+1/2}}{p_{i-1/2} - p_{i+1/2}}, \quad (p_{i+1/2} \leq p \leq p_{i-1/2}) \quad (I.42)
\]

\[
g_i = \bar{f}_i - f_{i+1/2}, \quad (I.43)
\]

\[
h_i = f_{i-1/2} - \bar{f}_i.
\]

Or equivalently, by using a new variable $\eta$ satisfying $\xi \Delta p_i + \eta \Delta p_i = 1$,

\[
\int_0^\xi R_i(\eta) \, d\xi = \frac{u_i \eta \cdot v_i (1 - \eta)}{u_i \eta + v_i (1 - \eta) + \text{sign}(\epsilon, u_i + v_i)} + \bar{f}_i(1 - \eta) \quad (I.44)
\]

where

\[
\eta = \frac{p_{i-1/2} - p}{p_{i-1/2} - p_{i+1/2}}, \quad (p_{i+1/2} \leq p \leq p_{i-1/2}) \quad (I.45)
\]

\[
u_i = \bar{f}_i - f_{i-1/2}, \quad (I.46)
\]

\[
\bar{f}_i = \frac{f_{i+1/2} - \bar{f}_i}{2}.
\]
Appendix II: Formulation of Long-lived Species

Prognostic equations for long-lived species are described here. The same notation is used as in the text except that $O^{1D} = O(1D)$; $pro_{no_cosmic}$ represents the NO production rate due to cosmic ray.

II-1 Daytime

\[
\frac{d[N_2O]}{dt} = -\left\{tj_4 + (b_{38} + b_{39})[O^{1D}]\right\}[N_2O]
\]

\[
\frac{d[CH_4]}{dt} = -\left\{tj_5 + a_{2et}[O^{1D}] + c_2[OH] + d_5[Cl]\right\}[CH_4]
\]

\[
\frac{d[H_2O]}{dt} = a_{23c}[H][HO_2] + \left\{a_{2et}[O^{1D}] + d_5[Cl] + tj_5\right\}[CH_4] + \left\{2c_2[CH_4] + a_{17}[HO_2] + a_{19}[H_2] + a_{30}[H_2O_2] + b_{27}[HNO_3] + b_{28}[HO_2NO_2]
\]

\[
+ d_0[CH_3Cl] + d_{11}[HCl] + d_{34}[HOCl] + e_{11}[HBr]\right\}[OH] - \left\{tj_3 + a_{1et}[O^{1D}]\right\}[H_2O]
\]

\[
\frac{d[NO_y]}{dt} = pro_{no_cosmic} + 2b_{39}[O^{1D}][N_2O] - 2b_6[N][NO] - \left\{het_1 + het_2\right\}[ClONO_2] - \left\{2het_3 + het_4\right\}[N_2O_5]
\]

\[
\frac{d[HNO_3]}{dt} = b_{22}[OH][NO_2][M] + g_1[ClONO_2] + 2g_2[N_2O_5]
\]

\[
+ g_3[BrONO_2] - \left\{tj_7 + b_{27}[OH]\right\}[HNO_3]
\]
Appendix II: Formulation of Long-lived Species

\[ \frac{d[N_2O_5]}{dt} = b_{12}[NO_3][NO_2][M] - \left\{ t_{j_{11}} + b_{32}[M] + het_3 + het_4 + g_2 \right\}[N_2O_5] \]

\[ \frac{d[Cl_y]}{dt} = \text{het}_2[ClONO_2] + \text{het}_4[N_2O_5] + \text{het}_5[HOC] + \text{het}_6[HOBr] + 4\left\{ t_{j_{26}} + d_{101}[O^{1D}] \right\}[CCl_4] + 3\left\{ t_{j_{27}} + d_{102}[O^{1D}] \right\}[CFCl_3] + 2\left\{ t_{j_{28}} + d_{103}[O^{1D}] \right\}[CF_2Cl_2] + \left\{ t_{j_{29}} + d_6[OH] \right\}[CH_3Cl] + t_{j_{31}}[CF_2ClBr] \]

\[ \frac{d[O_x]}{dt} = 2t_{j_1}[O_2] + t_{j_4}[N_2O] + t_{j_6}[NO_2] + t_{j_{14}}[OC\ell\ell] + t_{j_{18}}[CO_2] + t_{j_{23}}[NO] + t_{j_{24}}[NO_3] + a_{23}[H][HO_2] + b_6[N][NO] + b_7[O_2][N] \]

\[ - \left\{ 2\left( h_{k_1}[O][M] + h_{k_3}[O_3] \right)[O] + \left( a_{1_{et}}[H_2O] + a_{2_{et}}[CH_4] + a_{3_{et}}[H_2] + (b_{38} + b_{39})[N_2O] + d_{101}[CCl_4] + d_{102}[CFCl_3] + d_{103}[CF_2Cl_2] + e_{91}[CF_3Br] + e_{92}[CF_2ClBr] + e_{93}[CH_3Br] \right)[O^{1D}] \right\} + a_5[OH] + a_7[HO_2] + b_3[NO_2] + d_3[ClO] + d_{32}[ClONO_2] + d_{35}[HOC]\]

\[ + d_6[DClO] + e_3[BrO] + e_3[BrO] \right\}[O]\]

\[ + \left( a_2[H] + a_6[OH] + a_{6b}[HO_2] + b_4[NO] + b_9[NO_2] + d_2[Cl] + e_2[Br] \right)[O_3] \}

\[ \frac{d[CO]}{dt} = \left\{ a_{2_{et}}[O^{1D}] + d_5[Cl] + c_2[OH] + t_{j_5} \right\}[CH_4] + t_{j_{18}}[CO_2] - a_{3_{et}}[OH][CO] \]

\[ \frac{d[OC\ell\ell]}{dt} = \left( e_{5a}[BrO][ClO] - \left\{ d_{62}[OH] + d_{63}[Cl] + d_{64}[O] + d_{65}[NO] + e_8[Br] + t_{j_{14}} \right\}[OC\ell\ell] \right)\]
\[
\frac{d[CO_2]}{dt} = a_{36}[CO][OH] - t_{j_{18}}[CO_2]
\]
\[
\frac{d[HCl]}{dt} = \left\{ d_5[CH_4] + d_7[HO_2] + d_6[H_2] \right\}[Cl] - \left\{ t_{j_{16}} + d_{11}[OH] \right\}[HCl]
\]
\[
\frac{d[ClONO_2]}{dt} = d_{31}[NO_2][ClO] - \left\{ t_{j_{10}} + t_{j_{33}} + d_{32}[O] + het_1 + het_2 + g_1 \right\}[ClONO_2]
\]
\[
\frac{d[HOCl]}{dt} = d_{33}[HO_2][ClO] + d_{62}[OCIO][OH] + \left\{ het_1 + g_1 \right\}[ClONO_2] - \left\{ t_{j_{8}} + d_{34}[OH] + d_{35}[O] + d_{37}[Cl] + het_5 \right\}[HOCl]
\]
\[
\frac{d[Cl_2]}{dt} = \left\{ d_{37}[Cl] + het_5 \right\}[HOCl] + het_2[ClONO_2] - t_{j_{17}}[Cl_2]
\]
\[
\frac{d[H_2O_2]}{dt} = a_{27}[HO_2][HO_2] - \left\{ t_{j_{13}} + a_{30}[OH] \right\}[H_2O_2]
\]
\[
\frac{d[ClNO_2]}{dt} = d_{36}[Cl][NO_2][M] + het_4[N_2O_5] - t_{j_{19}}[ClNO_2]
\]
\[
\frac{d[HBr]}{dt} = e_{7}[HO_2][Br] - e_{11}[OH][HBr]
\]
Appendix II: Formulation of Long-lived Species

\[
\frac{d[BrONO_2]}{dt} = e_{13}[BrO][NO_2][M] - \left\{ t_{j20} + t_{j34} \right\} [BrONO_2] - g_3[BrONO_2]
\]

\[
\frac{d[NO_x]}{dt} = pro_{no\_cosmic} + \left\{ t_{j9} + b_{28}[OH] + b_{24}[M] \right\} [HO_2NO_2] + t_{j7}[HNO_3]
+ \left\{ 2t_{j11} + b_{32}[M] \right\} [N_2O_5] + 2b_{39}[O^{1D}][N_2O] + b_7[N][O_2] + b_{27}[HNO_3][OH]
+ \left\{ t_{j19} + d_{32}[O] \right\} [ClNO_2] + \left\{ t_{j10} + t_{j33} \right\} [ClONO_2] + \left\{ t_{j20} + t_{j34} \right\} [BrONO_2]
- \left\{ d_{31}[ClO] + b_{22}[OH] + b_{23}[HO_2] + 2b_{12}[NO_3] + d_{36}[Cl] + e_{13}[BrO] \right\} [NO_2][M]
- \left\{ b_6[N] + t_{j23} \right\} [NO]
\]

\[
\frac{d[HO_2NO_2]}{dt} = b_{23}[HO_2][NO_2][M] - \left\{ t_{j9} + b_{28}[OH] + b_{24}[M] \right\} [HO_2NO_2]
\]

\[
\frac{d[ClO_x]}{dt} = 2 \left\{ d_{61}[M] + t_{j15} \right\} [Cl_2O_2] + \left\{ t_{j10} + t_{j33} + d_{32}[O] \right\} [ClONO_2]
+ \left\{ t_{j8} + d_{34}[OH] + d_{35}[O] \right\} [HOCl]
+ \left\{ t_{j14} + d_{63}[Cl] + d_{64}[O] + d_{65}[NO] + e_8[Br] \right\} [OC1O]
+ \left\{ t_{j16} + d_{11}[OH] \right\} [HCl] + 2t_{j17}[Cl_2] + t_{j19}[ClNO_2] + t_{j21}[BrCl]
+ 4 \left\{ t_{j26} + d_{101}[O^{1D}] \right\} [CCl_4] + 3 \left\{ t_{j27} + d_{102}[O^{1D}] \right\} [CFCl_3]
+ 2 \left\{ t_{j28} + d_{103}[O^{1D}] \right\} [CF_2Cl_2]
- \left\{ d_{31}[NO_2] + 2d_{60}[ClO][M] + e_{5a}[BrO] + e_{5c}[BrO] + d_{33}[HO_2] \right\} [ClO]
- \left\{ d_{5}[CH_4] + d_{7}[HO_2] + d_{6}[H_2] + d_{36}[NO_2][M] + d_{37}[HOCl] \right\} [Cl]
\]
\[
\frac{d[BrO_x]}{dt} = \text{het}_6[HOBr] + t_{j22}[HOBr] + \left\{ t_{j20} + t_{j34} \right\}[BrONO_2] \\
+ e_{11}[OH][HBr] - e_7[Br][HO_2] - \left\{ e_{13}[NO_2][M] + e_{15}[HO_2] \right\}[BrO]
\]

\[
\frac{d[Cl_2O_2]}{dt} = d_{60}[ClO][ClO][M] - \left\{ t_{j15} + d_{61}[M] \right\}[Cl_2O_2]
\]

\[
\frac{d[HOBr]}{dt} = e_{15}[BrO][HO_2] + g_3[BrONO_2] - \text{het}_6[HOBr] - t_{j22}[HOBr]
\]

\[
\frac{d[CCl_4]}{dt} = -\left\{ t_{j26} + d_{101}[O^{1D}] \right\}[CCl_4]
\]

\[
\frac{d[CFCl_3]}{dt} = -\left\{ t_{j27} + d_{102}[O^{1D}] \right\}[CFCl_3]
\]

\[
\frac{d[CF_2Cl_3]}{dt} = -\left\{ t_{j28} + d_{103}[O^{1D}] \right\}[CF_2Cl_3]
\]

\[
\frac{d[Br_y]}{dt} = \left\{ t_{j32} + e_{a1}[O^{1D}] \right\}[CF_3Br] + \left\{ t_{j31} + e_{92}[O^{1D}] \right\}[CF_2ClBr] \\
+ \left\{ t_{j30} + e_{91}[O^{1D}] \right\}[CH_3Br]
\]
\[
\begin{align*}
\frac{d[CH_3Cl]}{dt} &= -\left\{ t_{j29} + d_9[OH] \right\} [CH_3Cl] \\
\frac{d[CH_3Br]}{dt} &= -\left\{ t_{j30} + e_{93}[O^{1D}] \right\} [CH_3Br] \\
\frac{d[CH_2ClBr]}{dt} &= -\left\{ t_{j31} + e_{92}[O^{1D}] \right\} [CH_2ClBr] \\
\frac{d[CF_3Cl]}{dt} &= -\left\{ t_{j32} + e_{91}[O^{1D}] \right\} [CF_3Cl] \\
\frac{d[HNO_3]_{(s)}}{dt} &= \left\{ het_1 + het_2 \right\} [ClONO_2] + \left\{ 2het_3 + het_4 \right\} [N_2O_5] \\
\frac{d[H_2O]_{(s)}}{dt} &= het_5[HOCl] + het_6[HOBr] - het_1[ClONO_2] - het_3[N_2O_5] \\
\frac{d[HCl]_{(s)}}{dt} &= -het_2[ClONO_2] - het_4[N_2O_5] - het_5[HOCl] - het_6[HOBr]
\end{align*}
\]

II-2 Nighttime

The prognostic equations for long-lived species during nighttime can be written in simplified forms because all photolysis rates are zero, and because some short-lived species are set to zero for the nighttime calculation.

\[
\frac{d[N_2O]}{dt} = 0
\]
\[
\frac{d[CH_4]}{dt} = 0 \\
\frac{d[H_2O]}{dt} = 0 \\
\frac{d[NO_y]}{dt} = \text{pro_no_cosmic} - \left\{ \text{het}_1 + \text{het}_2 \right\}[\text{ClONO}_2] - \left\{ 2\text{het}_3 + \text{het}_4 \right\}[\text{N}_2\text{O}_5] \\
\frac{d[HNO_3]}{dt} = 2g_2[\text{N}_2\text{O}_5] + g_1[\text{ClONO}_2] + g_3[\text{BrONO}_2] \\
\frac{d[\text{N}_2\text{O}_5]}{dt} = b_{12}[\text{NO}_3][\text{NO}_2][\text{M}] - \left\{ b_{32}[\text{M}] + \text{het}_3 + \text{het}_4 + g_2 \right\}[\text{N}_2\text{O}_5] \\
\frac{d[\text{Cl}_y]}{dt} = \text{het}_2[\text{ClONO}_2] + \text{het}_4[\text{N}_2\text{O}_5] + \text{het}_5[\text{HOCl}] + \text{het}_6[\text{HOBr}] \\
\frac{d[O_x]}{dt} = -b_9[\text{NO}_2][\text{O}_3] \\
\frac{d[CO]}{dt} = 0 \\
\frac{d[\text{OCIO}]}{dt} = e_{5a}[\text{BrO}][\text{ClO}] \\
\frac{d[\text{CO}_2]}{dt} = 0 \\
\frac{d[HCl]}{dt} = 0 \\
\frac{d[\text{ClONO}_2]}{dt} = d_31[\text{NO}_2][\text{ClO}] - \left\{ \text{het}_1 + \text{het}_2 + g_1 \right\}[\text{ClONO}_2] \\
\frac{d[\text{HOCl}]}{dt} = \text{het}_1[\text{ClONO}_2] + g_1[\text{ClONO}_2] - \text{het}_5[\text{HOCl}] 
\]
Appendix II: Formulation of Long-lived Species

\[
\frac{d[Cl_2]}{dt} = het_2[ClONO_2] + het_5[HOCl]
\]

\[
\frac{d[H_2O_2]}{dt} = 0
\]

\[
\frac{d[ClNO_2]}{dt} = het_4[N_2O_5]
\]

\[
\frac{d[HBr]}{dt} = 0
\]

\[
\frac{d[BrONO_2]}{dt} = e_{13}[BrO][NO_2][M] - g_3[BrONO_2]
\]

\[
\frac{d[NO_x]}{dt} = pro_{no_{cosmic}} + 2b_{32}[M][N_2O_5] + b_{24}[HO_2NO_2][M] - \left\{b_{12}[NO_3][M] + d_{31}[ClO][M] + e_{13}[BrO][M]\right\}[NO_2]
\]

\[
\frac{d[HO_2NO_2]}{dt} = -b_{24}[M][HO_2NO_2]
\]

\[
\frac{d[ClO_x]}{dt} = 2d_{61}[M][Cl_2O_2] - \left\{d_{31}[NO_2][M] + 2d_{60}[ClO][M] + e_{5a}[BrO] + e_{5c}[BrO]\right\}[ClO]
\]

\[
\frac{d[BrO_x]}{dt} = het_6[HOBr] - e_{13}[NO_2][BrO][M]
\]

\[
\frac{d[Cl_2O_2]}{dt} = d_{60}[ClO][ClO][M] - d_{61}[M][Cl_2O_2]
\]

\[
\frac{d[HOBr]}{dt} = -het_6[HOBr] + g_3[BrONO_2]
\]

\[
\frac{d[CCl_4]}{dt} = 0
\]

\[
\frac{d[CFCl_3]}{dt} = 0
\]

\[
\frac{d[CF_2Cl_3]}{dt} = 0
\]

\[
\frac{d[Br_y]}{dt} = 0
\]
\[
\begin{align*}
\frac{d[CH_3Cl]}{dt} &= 0 \\
\frac{d[CH_3Br]}{dt} &= 0 \\
\frac{d[CH_2ClBr]}{dt} &= 0 \\
\frac{d[CF_3Cl]}{dt} &= 0 \\
\frac{d[HNO_3](s)}{dt} &= \left\{ het_1 + het_2 \right\}[ClONO_2] + \left\{ 2het_3 + het_4 \right\}[N_2O_5] \\
\frac{d[H_2O](s)}{dt} &= het_5[HOCl] + het_6[HOBr] - het_1[ClONO_2] - het_3[N_2O_5] \\
\frac{d[HCl](s)}{dt} &= -het_2[ClONO_2] - het_4[N_2O_5] - het_5[HOCl] - het_6[HOBr]
\end{align*}
\]
Appendix III: Formulation of Short-lived Species

III-1. Daytime

III-1-1 $HO_x$ Family and $N$

Instantaneous equilibrium is assumed for $HO_x(\equiv H + OH + HO_2)$ and its members. Then, the change rate of $HO_x$ can be set to zero

$$
\frac{d[HO_x]}{dt} = 2a_{1et}[O^{1D}][H_2O] + a_{2et}[O^{1D}][CH_4] \\
+ 2a_{3et}[O^{1D}][H_2] - 2a_{23b}[H][HO_2] \\
- 2a_{23c}[H][HO_2] - 2a_{17}[OH][HO_2] \\
+ a_{24}[H_2][O] - 2a_{27}[HO_2][HO_2] \\
- b_{27}[HNO_3][OH] - b_{28}[HO_2NO_2][OH] \\
- b_{22}[NO_2][OH][M] - b_{23}[NO_2][HO_2][M] \\
+ b_{24}[HO_2NO_2][M] - c_2[CH_4][OH] \\
+ d_0[CH_3Cl][OH] + d_6[Cl][H_2] \\
- d_7[Cl][HO_2] - d_{11}[HCl][OH] \\
- d_{33}[ClO][HO_2] - d_{34}[HOCl][OH] \\
+ d_{35}[HOCl][O] + d_{37}[HOCl][Cl] \\
- d_{62}[OCIO][OH] - e_7[Br][HO_2] \\
- e_{11}[HBr][OH] - e_{15}[BrO][HO_2] \\
+ 2t_{j3}[H_2O] + t_{j5}[CH_4] + t_{j7}[HNO_3] \\
+ t_{j8}[HOCl] + t_{j9}[HO_2NO_2] \\
+ 2t_{j13}[H_2O_2] + t_{j16}[HCl] + t_{j22}[HOBr] = 0. \quad (III.1)
$$

Arranging Eq.(III.1) with the use of $[H]/[OH]$ and $[HO_2]/[OH]$, we get a quadratic function of $[OH]$

$$
\frac{d[HO_x]}{dt} = - \left\{ 2a_{23b}\frac{[H]}{[OH]}\frac{[HO_2]}{[OH]} + 2a_{23c}\frac{[H]}{[OH]}\frac{[HO_2]}{[OH]} \\
+ 2a_{17}\frac{[HO_2]}{[OH]} + 2a_{27}\frac{[HO_2]}{[OH]} \right\}[OH]^2 \\
- b_{22}[NO_2][M] + b_{23}[NO_2]\frac{[HO_2]}{[OH]}[M] \\
+ b_{27}[HNO_3] + b_{28}[HO_2NO_2] + c_2[CH_4] \\
+ d_0[CH_3Cl] + d_7[Cl]\frac{[HO_2]}{[OH]} + d_{11}[HCl] \right\}
$$
Appendix III: Formulation of Short-lived Species

\[ + d_{33}[ClO] \frac{[HO_2]}{[OH]} + d_{34}[HOCl] \]
\[ + d_{62}[OClO] + e_7[Br] \frac{[HO_2]}{[OH]} + e_{11}[HBr] \]
\[ + e_{15}[BrO] \frac{[HO_2]}{[OH]} \}
\[ = 0. \]

\( (III.2) \)

The change rates of \( HO_2 \) and \( H \) are also equal to zero

\[ \frac{[dHO_2]}{dt} \]
\[ = - (a_{23a} + a_{23b} + a_{23c})[H][HO_2] \]
\[ + a_6[OH][O_3] - a_{6b}[HO_2][O_3] \]
\[ - a_7[HO_2][O] - a_{17}[OH][HO_2] \]
\[ - a_{26}[HO_2][NO] - 2a_{27}[HO_2][HO_2] \]
\[ + a_{30}[OH][H_2O_2] + a_1[H][O_2][M] \]
\[ - b_{23}[NO_2][HO_2][M] + b_{24}[HO_2NO_2][M] \]
\[ + d_8[ClO][OH] - d_7[Cl][HO_2] \]
\[ - d_{33}[ClO][HO_2] - e_7[Br][HO_2] \]
\[ - e_{15}[BrO][HO_2] - t_{j9}[HO_2NO_2] \]
\[ = 0. \]

\( (III.3) \)

\[ \frac{[dH]}{dt} \]
\[ = a_{3et}[O^{1D}][H_2] - a_{23}[H][HO_2] \]
\[ - a_2[H][O_3] + a_5[OH][O] \]
\[ + a_{19}[OH][H_2] + a_{24}[H_2][O] \]
\[ + a_{36}[OH][CO] - a_1[H][O_2][M] \]
\[ + d_6[Cl][H_2] + t_{j5}[CH_4] \]
\[ = 0. \]

\( (III.4) \)
From Eqs. (III.3) and (III.4), we get

\[
\frac{[HO_2]}{[OH]} = \left\{ a_6 [O_3] + a_1 [O_2] [M] \frac{[H]}{[OH]} + d_8 [ClO] + a_{30} [H_2O_2] \right\} \\
\left/ \left\{ a_{23} [H] + a_{69} [O_3] + a_7 [O] + a_{26} [NO] + a_{17} [OH] + b_{23} [NO_2] [M] \\
+ d_7 [Cl] + d_{33} [ClO] + e_7 [Br] + e_{15} [BrO] + 2a_{27} [HO_2] \right\}, \tag{III.5} \right.
\]

\[
\frac{[H]}{[OH]} = \left\{ a_5 [O] + a_{19} [H_2] + a_{36} [CO] \right\} \left/ \left\{ a_1 [O_2] [M] + a_2 [O_3] + a_{23} [HO_2] \right\} \right. \right. \tag{III.6}
\]

When Eqs. (III.5) and (III.6) are calculated, all the coefficients of Eq. (III.2) are then given. The quadratic equation thus can be solved readily.

Instantaneous equilibrium is also assumed for \( N \) and thus its change rate is expressed by

\[
\frac{d[N]}{dt} = t_{j23} [NO] - b_6 [N] [NO] - b_7 [N] [O_2] = 0. \tag{III.7} \]

Then,

\[
[N] = \frac{t_{j23} [NO]}{b_6 [NO] + b_7 [O_2]} \tag{III.8} \]

III-1-2 \( NO_x \) Family

The reduce-Jacobian method is used for \( NO_x \) family. The change rates of all the members in daytime are formulated to be linear for the values at \( t + \Delta t \)

\[
\frac{[NO]^{t+\Delta t} - [NO]^t}{\Delta t} = \left\{ - a_{26} [HO_2] - b_4 [O_3] - b_6 [N] - d_4 [ClO] \\
- d_{65} [OCIO] - e_4 [BrO] - t_{j23} \right\} [NO]^{t+\Delta t} \\
+ \left\{ b_3 [O] + t_{j2} \right\} [NO_2]^{t+\Delta t} \\
+ \left\{ t_{j25} \right\} [NO_3]^{t+\Delta t} 
\]
Appendix III: Formulation of Short-lived Species

\[ [NO_2]^{t+\Delta t} - [NO_2]^t \]
\[ \frac{\Delta t}{\Delta t} = \left\{ a_{26}[HO_2] + b_4[O_3] + d_4[ClO] \right. \]
\[ + d_{65}[OCIO] + e_4[BrO] + \left. \right\} [NO]^{t+\Delta t} \]
\[ + \left\{ - b_9[O] - b_9[O_3] \right. \]
\[ - 0.5b_{12}[NO_3]^t - b_{22}[OH] \]
\[ - b_{23}[HO_2] - d_{31}[ClO] \]
\[ - d_{36}[Cl]- e_{13}[BrO] - t_{j6} \right\} [NO_2]^{t+\Delta t} \]
\[ + \left\{ - (1/2)b_{12}[NO_2]^t + t_{j24} \right\} [NO_3]^{t+\Delta t} \]
\[ + \left\{ (b_{24}[M] + b_{28}[OH])[HO_2]NO_2 \right. \]
\[ + b_{32}[N_2O_5][M] + t_{j7}[HNO_3] \]
\[ + t_{j9}[HO_2NO_2] + t_{j11}[N_2O_5] \]
\[ + t_{j19}[ClNO_2] + t_{j33}[ClONO_2] \]
\[ + t_{j34}[BrONO_2] \right\}, \]
\[ (III.9a) \]

\[ [NO_3]^{t+\Delta t} - [NO_3]^t \]
\[ \frac{\Delta t}{\Delta t} = \left\{ 0 \right\} \]
\[ + \left\{ b_9[O_3] - 0.5b_{12}[NO_3]^t \right\} [NO]^{t+\Delta t} \]
\[ + \left\{ - t_{j24} - t_{j25} - 0.5b_{12}[NO_2]^t \right\} [NO_2]^{t+\Delta t} \]
\[ + \left\{ b_{27}[HNO_3][OH] + b_{32}[N_2O_5][M] \right. \]
\[ + d_{32}[ClONO_2][O] + t_{j10}[ClONO_2] \]
\[ + t_{j11}[N_2O_5] + t_{j20}[BrONO_2] \right\}. \]
\[ (III.9b) \]

Eqs. (III.9a, b, c) can be formally written as a matrix equation of 3 × 3
\[
\frac{[\text{NO}]+\Delta t - [\text{NO}]}{\Delta t}
= A_{11}[\text{NO}]^{t+\Delta t} + A_{12}[\text{NO}_2]^{t+\Delta t} + A_{13}[\text{NO}_3]^{t+\Delta t} + A_{14},
\]
\[
\frac{[\text{NO}_2]^{t+\Delta t} - [\text{NO}_2]}{\Delta t}
= A_{21}[\text{NO}]^{t+\Delta t} + A_{22}[\text{NO}_2]^{t+\Delta t} + A_{23}[\text{NO}_3]^{t+\Delta t} + A_{24},
\]
\[
\frac{[\text{NO}_3]^{t+\Delta t} - [\text{NO}_3]}{\Delta t}
= A_{31}[\text{NO}]^{t+\Delta t} + A_{32}[\text{NO}_2]^{t+\Delta t} + A_{33}[\text{NO}_3]^{t+\Delta t} + A_{34},
\]

or equivalently, where \( \delta_{ij} \) is Kronecker’s delta.

\[
\begin{pmatrix}
1 - A_{11}\Delta t & -A_{12}\Delta t & -A_{13}\Delta t \\
-A_{21}\Delta t & 1 - A_{22}\Delta t & -A_{23}\Delta t \\
-A_{31}\Delta t & -A_{32}\Delta t & 1 - A_{33}\Delta t
\end{pmatrix}
\begin{pmatrix}
[\text{NO}]^{t+\Delta t} \\
[\text{NO}_2]^{t+\Delta t} \\
[\text{NO}_3]^{t+\Delta t}
\end{pmatrix}
= \begin{pmatrix}
[\text{NO}]^{t+\Delta t} \\
[\text{NO}_2]^{t+\Delta t} \\
[\text{NO}_3]^{t+\Delta t}
\end{pmatrix}
+ \begin{pmatrix}
A_{14}\Delta t \\
A_{24}\Delta t \\
A_{34}\Delta t
\end{pmatrix}.
\] (III.10)

It is straightforward to obtain the ratios at \( t + \Delta \), for example \( \left( \frac{[\text{NO}_2]}{[\text{NO}]} \right)^{t+\Delta t} \) and
\( \left( \frac{[\text{NO}_3]}{[\text{NO}]} \right)^{t+\Delta t} \), by solving Eq.(III.10). The final form of the members are then

\[
[\text{NO}]^{t+\Delta t} = \frac{[\text{NO}_x]^{t+\Delta t}}{1 + \left( \frac{[\text{NO}_2]}{[\text{NO}]} \right)^{t+\Delta t} + \left( \frac{[\text{NO}_3]}{[\text{NO}]} \right)^{t+\Delta t}},
\] (III.11a)

\[
[\text{NO}_2]^{t+\Delta t} = \left( \frac{[\text{NO}_2]}{[\text{NO}]} \right)^{t+\Delta t} [\text{NO}]^{t+\Delta t},
\] (III.11b)

\[
[\text{NO}_3]^{t+\Delta t} = \left( \frac{[\text{NO}_3]}{[\text{NO}]} \right)^{t+\Delta t} [\text{NO}]^{t+\Delta t}.
\] (III.11c)
Appendix III: Formulation of Short-lived Species

As for \( O_x, ClO_x \) and \( BrO_x \), their change rate equations are expressed by similar matrix equations as given below, and thereby the solutions can be readily calculated as Eqs. (III.11a, b, c).

III-1-3 \( O_x \) Family

\[
\frac{[O_3]^{t+\Delta t} - [O_3]^t}{\Delta t} = \begin{cases} 
-0.5hk_3[O]^t - a_2[H] - a_6[OH] \\
- a_{6b}[HO_2] - b_4[NO] - b_9[NO_2] \\
- d_2[Cl] - e_2[Br] - t_{j2} - t_{j12} \end{cases}
\] [\( O_3 \)^{t+\Delta t}]

\[
+ \left\{ \begin{array}{c}
hk_2[O_2][M] - (1/2)hk_3[O_3]^t \\
0 \end{array} \right\}
\] [\( O \)^{t+\Delta t}]

\[
+ \left\{ \begin{array}{c}
0 \\
0 \end{array} \right\}
\] [\( O^{1D} \)^{t+\Delta t}]

(III.12a)

\[
\frac{[O]^{t+\Delta t} - [O]^t}{\Delta t} = \begin{cases} 
-0.5hk_3[O]^t + t_{j2} \end{cases}
\] [\( O_3 \)^{t+\Delta t}]

\[
+ \left\{ \begin{array}{c}
-0.5hk_3[O_3]^t - 2hk_1[O]^t[M] \\
hk_2[O_2][M] - a_5[OH] - a_7[HO_2] \\
a_{24}[H_2] - b_3[NO_2] - d_3[ClO] \\
d_{32}[ClONO_2] - d_{35}[HOCl] \\
d_{64}[OClO] - e_3[BrO] \end{array} \right\}
\] [\( O \)^{t+\Delta t}]

\[
+ \left\{ \begin{array}{c}
hk_4[N_2] + hk_5[O_2] \\
a_{23c}[H][HO_2] + b_6[N][NO] \\
+ b_7[N][O_2] + 2t_{j1}[O_2] + t_{j6}[NO_2] \\
t_{j14}[OCIO] + t_{j18}[CO_2] \\
t_{j23}[NO] + t_{j24}[NO_3] \end{array} \right\}
\] [\( O^{1D} \)^{t+\Delta t}]

(III.12b)

\[
\frac{[O^{1D}]^{t+\Delta t} - [O^{1D}]^t}{\Delta t} = \left\{ t_{j12} \right\}
\] [\( O_3 \)^{t+\Delta t}

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\[
\begin{align*}
+ \left\{ \begin{array}{c}
0 \\
- hk_4[N_2] - hk_5[O_2] \\
- a_{1et}[H_2O] - a_{2et}[CH_4] \\
- a_{3et}[H_2] - b_{38}[N_2O] \\
b_{39}[N_2O] - d_{101}[CCl_4] \\
- d_{102}[CFCl_3] - d_{103}[CF_2Cl_2] \\
- e_{91}[CF_3Br] - e_{92}[CF_2ClBr] \\
- e_{93}[CH_3Br] \\
\end{array} \right\} & \quad [O]^{t+\Delta t} \\
\begin{array}{c}
+ \{ t_{j4}[N_2O] \} \\
\end{array} & \quad [O^{1D}]^{t+\Delta t} \\
\end{align*}
\]

**III-1-4 ClO\textsubscript{x} Family**

\[
\begin{align*}
[Cl]^{t+\Delta t} - [Cl]^t \\
\Delta t \\
= \left\{ \begin{array}{c}
- d_2[O_3] - d_5[CH_4] - d_6[H_2] \\
- d_7[HO_2] - d_36[NO_2][M] \\
- d_{37}[HOCl] - d_{63}[OCIO] \\
\end{array} \right\} & \quad [Cl]^{t+\Delta t} \\
+ \left\{ d_3[O] + d_4[NO] \\
+ d_8[OH] + e_{5b}[BrO] \right\} & \quad [ClO]^{t+\Delta t} \\
+ \left\{ \begin{array}{c}
(d_9[CH_3Cl] + d_{11}[HCl]) [OH] \\
+ (4d_{101}[CCl_4] + 3d_{102}[CFCl_3] \\
+ 2d_{103}[CF_2Cl_2] \\
+ e_{92}[CF_2ClBr] \end{array} \right\} [O^{1D}] \\
+ t_{j_8}[HOCl] + t_{j_9}[ClONO_2] \\
+ 2t_{j_8}[Cl_2O_2] + t_{j_9}[HCl] \\
+ 2t_{j_7}[Cl_2] + t_{j_9}[ClNO_2] \\
+ t_{j_21}[BrCl] + 4t_{j_26}[CCl_4] \\
+ 3t_{j_27}[CFCl_3] + 2t_{j_28}[CF_2Cl_2] \\
+ t_{j_29}[CH_3Cl] + t_{j_31}[CF_2ClBr] \right\}, & \quad (III.13a)
\end{align*}
\]
Appendix III: Formulation of Short-lived Species

\[
\frac{[ClO]^{t+\Delta t} - [ClO]^t}{\Delta t}
= \left\{ d_2[O_3] + 2d_{63}[OClO] \right\} [Cl]^{t+\Delta t}
+ \left\{ - d_3[O] - d_4[NO] - d_8[OH] \\
- d_{31}[NO_2][M] - d_{33}[HO_2] \\
- 2d_{60}[ClO]^t \\
- (e_{5a} + e_{5b} + e_{5c})[BrO] \right\} [ClO]^{t+\Delta t}
+ \left\{ d_{32}[ClONO_2][O] + d_{34}[HOCl][OH] \\
+ d_{35}[HOCl][O] + 2d_{61}[M][Cl_2O_2] \\
+ d_{64}[OCIO][O] + d_{65}[OCIO][NO] \\
+ e_8[Br][OCIO] + tj_{33}[ClONO_2] \\
+ tj_{14}[OCIO] \right\}.
\] (III.13b)

III-1-5 BrO_x Family

\[
\frac{[Br]^{t+\Delta t} - [Br]^t}{\Delta t}
= \left\{ - e_2[O_3] - e_7[HO_2] - e_8[OCIO] \right\} [Br]^{t+\Delta t}
+ \left\{ e_3[O] + e_4[NO] \\
+ (e_{5a} + e_{5b})[ClO] + 2e_6[BrO]^t \right\} [BrO]^{t+\Delta t}
+ \left\{ tj_{21} \right\} [BrCl]^{t+\Delta t}
+ \left\{ e_{11}[HBr][OH] \\
+ \left( e_{91}[CF_3Br] + e_{92}[CF_2ClBr] \\
+ e_{93}[CH_3Br] \right)[O^{1D}] \\
+ tj_{20}[BrONO_2] + tj_{22}[HOBr] \\
+ tj_{31}[CF_2ClBr] + tj_{32}[CH_3Br] \right\},
\] (III.14a)
\[
\begin{align*}
&= \left\{ e_2[O_3] + e_8[OCIO] \right\} + \left\{ -e_3[O] - e_4[NO] \right. \\
&\quad - (e_{5a} + e_{5b} + e_{5c})[ClO] \\
&\quad - 2e_6[BrO]' - e_{13}[NO_2][M] \\
&\quad - e_{15}[HO_2] \right\} + \left\{ 0 \right\} + \left\{ t_{j34}[BrONO_2] \right\}, \\
&\frac{[BrCl]^{t+\Delta t} - [BrCl]^t}{\Delta t} \\
&= \left\{ 0 \right\} + \left\{ e_{5c}[ClO] \right\} + \left\{ -t_{j21} \right\} + \left\{ het_6[HOBr] \right\}. \\
&\quad (III.14b) \\
&\quad (III.14c)
\end{align*}
\]

III-2 Nighttime

During nighttime only \((NO_2, NO_3)\) and \((BrO, BrCl)\) are solved with the reduced Jacobian method, while others are set to zero or a certain very small, virtually zero, value \((\varepsilon)\).

\[
\begin{align*}
[H] &= 0, \\
[OH] &= \varepsilon, \\
[HO_2] &= \varepsilon, \\
[N] &= \varepsilon, \\
[NO] &= \varepsilon, \\
[O^{1D}] &= \varepsilon, \\
[O^{3P}] &= \varepsilon, \\
[O_3] &= O_x - 2\varepsilon, \\
[Cl] &= \varepsilon, \\
[ClO] &= [ClO_2] - \varepsilon, \\
[Br] &= \varepsilon,
\end{align*}
\]

\((III.15)\)

The remaining species, \((NO_2, NO_3)\) and \((BrO, BrCl)\), are represented by \(2\times2\) matrices.
\[
\frac{[NO_2]^{t+\Delta t} - [NO_2]^t}{\Delta t} = \left\{ -b_9[O_3] - (1/2)b_{12}[NO_3]^t - d_{31}[ClO] - e_{13}[BrO] \right\} [NO_2]^{t+\Delta t} \\
+ \left\{ - (1/2)b_{12}[NO_2]^t \right\} [NO_3]^{t+\Delta t} \\
+ \left\{ b_{24}[HO_2NO_2][M] + b_{32}[N_2O_5][M] \right\}
\]  

(III.16a)

\[
\frac{[NO_3]^{t+\Delta t} - [NO_3]^t}{\Delta t} = \left\{ b_9[O_3] - (1/2)b_{12}[NO_3]^t \right\} [NO_2]^{t+\Delta t} \\
+ \left\{ - (1/2)b_{12}[NO_2]^t \right\} [NO_3]^{t+\Delta t} \\
+ \left\{ b_{32}[N_2O_5][M] \right\}
\]

(III.16b)

\[
\frac{[BrO]^{t+\Delta t} - [BrO]^t}{\Delta t} = \left\{ -(e_{5a} + e_{5b} + e_{5c})[ClO] - 2e_6[BrO]^t - e_{13}[NO_2][M] \right\} [BrO]^{t+\Delta t} \\
+ \left\{ 0 \right\} [BrCl]^{t+\Delta t} \\
+ \left\{ 0 \right\}
\]

(III.17a)

\[
\frac{[BrCl]^{t+\Delta t} - [BrCl]^t}{\Delta t} = \left\{ e_{5c}[ClO] \right\} [BrO]^{t+\Delta t} \\
+ \left\{ 0 \right\} [BrCl]^{t+\Delta t} \\
+ \left\{ het_6[HOBr] \right\}
\]

(III.17b)
Tables and Figures
Table 1. Names of species

<table>
<thead>
<tr>
<th>Long-lived</th>
</tr>
</thead>
<tbody>
<tr>
<td>01...$N_2O$</td>
</tr>
<tr>
<td>04...$NO_y$</td>
</tr>
<tr>
<td>07...$Cl_y$</td>
</tr>
<tr>
<td>10...$OClO$</td>
</tr>
<tr>
<td>13...$HCl$</td>
</tr>
<tr>
<td>16...$Cl_2$</td>
</tr>
<tr>
<td>19...$HBr$</td>
</tr>
<tr>
<td>22...$HO_2NO_2$</td>
</tr>
<tr>
<td>25...$Cl_2O_2$</td>
</tr>
<tr>
<td>28...$CFCl_3$ ($CFC-11$)</td>
</tr>
<tr>
<td>31...$CH_3Cl$</td>
</tr>
<tr>
<td>34...$CF_3Br$ ($Halon-1301$)</td>
</tr>
<tr>
<td>02...$CH_4$</td>
</tr>
<tr>
<td>05...$HNO_3$</td>
</tr>
<tr>
<td>08...$O_x$</td>
</tr>
<tr>
<td>11...$CO_2$</td>
</tr>
<tr>
<td>14...$ClONO_2$</td>
</tr>
<tr>
<td>17...$H_2O_2$</td>
</tr>
<tr>
<td>20...$BrONO_2$</td>
</tr>
<tr>
<td>23...$ClO_x$</td>
</tr>
<tr>
<td>26...$HOBr$</td>
</tr>
<tr>
<td>29...$CF_2Cl_2$ ($CFC-12$)</td>
</tr>
<tr>
<td>32...$CH_3Br$</td>
</tr>
<tr>
<td>35...$COF_2$</td>
</tr>
<tr>
<td>03...$H_2O$</td>
</tr>
<tr>
<td>06...$N_2O_5$</td>
</tr>
<tr>
<td>09...$CO$</td>
</tr>
<tr>
<td>12...Passive tracer</td>
</tr>
<tr>
<td>15...$HOCl$</td>
</tr>
<tr>
<td>18...$ClNO_2$</td>
</tr>
<tr>
<td>21...$NO_x$</td>
</tr>
<tr>
<td>24...$BrO_x$</td>
</tr>
<tr>
<td>27...$CCl_4$ ($CFC-10$)</td>
</tr>
<tr>
<td>30...$Br_y$</td>
</tr>
<tr>
<td>33...$CF_3ClBr$ ($Halon-1211$)</td>
</tr>
<tr>
<td>36...$HF$</td>
</tr>
</tbody>
</table>

$O_x = O_3 + O(^3P) + O(^1D)$

$ClO_x = Cl + ClO$

$Cl_y = ClO_x + OClO + 2Cl_2O_2 + HCl + ClONO_2 + HOCl + 2Cl_2$
+ $ClNO_2 + BrCl$

$NO_x = NO + NO_2 + NO_3$

$NO_y = NO_x + N + NO_3 + HNO_3 + 2N_2O_5 + HO_2NO_2 + ClONO_2$
+ $ClNO_2 + BrONO_2$

$BrO_x = Br + BrO + BrCl$

$Br_y = BrO_x + HBr + HOBr + BrONO_2$

<table>
<thead>
<tr>
<th>Short-lived</th>
</tr>
</thead>
<tbody>
<tr>
<td>01...$O(^1D)$</td>
</tr>
<tr>
<td>04...$O(^3P)$</td>
</tr>
<tr>
<td>07...$NO_2$</td>
</tr>
<tr>
<td>10...$N$</td>
</tr>
<tr>
<td>13...$NO_3$</td>
</tr>
<tr>
<td>02...$OH$</td>
</tr>
<tr>
<td>05...$O_3$</td>
</tr>
<tr>
<td>08...$NO$</td>
</tr>
<tr>
<td>11...$ClO$</td>
</tr>
<tr>
<td>14...$BrCl$</td>
</tr>
<tr>
<td>03...$Cl$</td>
</tr>
<tr>
<td>06...$HO_2$</td>
</tr>
<tr>
<td>09...$Br$</td>
</tr>
<tr>
<td>12...$BrO$</td>
</tr>
<tr>
<td>15...$H$</td>
</tr>
</tbody>
</table>
### Table 2a. Gas Phase Reactions

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxygen reactions</td>
</tr>
<tr>
<td>$h_{k_1}$</td>
<td>$O + O + M \rightarrow O_2 + M$</td>
</tr>
<tr>
<td>$h_{k_2}$</td>
<td>$O + O_2 + M \rightarrow O_3 + M$</td>
</tr>
<tr>
<td>$h_{k_3}$</td>
<td>$O + O_3 \rightarrow O_2 + O_2$</td>
</tr>
<tr>
<td>$h_{k_4}$</td>
<td>$O^{1D} + N_2 \rightarrow O + N_2$</td>
</tr>
<tr>
<td>$h_{k_5}$</td>
<td>$O^{1D} + O_2 \rightarrow O + O_2$</td>
</tr>
<tr>
<td></td>
<td>Odd hydrogen reactions</td>
</tr>
<tr>
<td>$a_1$</td>
<td>$H + O_2 + M \rightarrow HO_2 + M$</td>
</tr>
<tr>
<td>$a_{1et}$</td>
<td>$O^{1D} + H_2O \rightarrow OH + OH$</td>
</tr>
<tr>
<td>$a_2$</td>
<td>$H + O_3 \rightarrow OH + O_2$</td>
</tr>
<tr>
<td>$a_{2et}$</td>
<td>$O^{1D} + CH_4 \rightarrow OH + CO + H_2O + products$</td>
</tr>
<tr>
<td>$a_{3et}$</td>
<td>$O^{1D} + H_2 \rightarrow OH + H$</td>
</tr>
<tr>
<td>$a_5$</td>
<td>$OH + O \rightarrow H + O_2$</td>
</tr>
<tr>
<td>$a_6$</td>
<td>$OH + O_3 \rightarrow HO_2 + O_2$</td>
</tr>
<tr>
<td>$a_{6b}$</td>
<td>$HO_2 + O_3 \rightarrow OH + 2O_2$</td>
</tr>
<tr>
<td>$a_7$</td>
<td>$HO_2 + O \rightarrow OH + O_2$</td>
</tr>
<tr>
<td>$a_{17}$</td>
<td>$OH + HO_2 \rightarrow H_2O + O_2$</td>
</tr>
<tr>
<td>$a_{19}$</td>
<td>$OH + H_2 \rightarrow H_2O + H$</td>
</tr>
<tr>
<td>$a_{23a}$</td>
<td>$H + HO_2 \rightarrow OH + OH$</td>
</tr>
<tr>
<td>$a_{23b}$</td>
<td>$H + HO_2 \rightarrow H_2 + O_2$</td>
</tr>
<tr>
<td>$a_{23c}$</td>
<td>$H + HO_2 \rightarrow H_2O + O$</td>
</tr>
<tr>
<td>$a_{24}$</td>
<td>$H_2 + O \rightarrow OH + H$</td>
</tr>
<tr>
<td>$a_{26}$</td>
<td>$HO_2 + NO \rightarrow NO_2 + OH$</td>
</tr>
<tr>
<td>$a_{27}$</td>
<td>$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$</td>
</tr>
<tr>
<td>$a_{30}$</td>
<td>$OH + H_2O_2 \rightarrow H_2O + HO_2$</td>
</tr>
<tr>
<td>$a_{36}$</td>
<td>$OH + CO \rightarrow CO_2 + H$</td>
</tr>
</tbody>
</table>
Table 2b. Gas Phase Reactions

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odd nitrogen reactions</td>
<td></td>
</tr>
<tr>
<td>$b_3$</td>
<td>$NO_2 + O$ $\rightarrow$ $NO + O_2$</td>
</tr>
<tr>
<td>$b_4$</td>
<td>$NO + O_3$ $\rightarrow$ $NO_2 + O_2$</td>
</tr>
<tr>
<td>$b_6$</td>
<td>$N + NO$ $\rightarrow$ $N_2 + O$</td>
</tr>
<tr>
<td>$b_7$</td>
<td>$N + O_2$ $\rightarrow$ $NO + O$</td>
</tr>
<tr>
<td>$b_9$</td>
<td>$NO_3 + O_3$ $\rightarrow$ $NO_3 + O_2$</td>
</tr>
<tr>
<td>$b_{12}$</td>
<td>$NO_2 + NO_3 + M$ $\rightarrow$ $N_2O_5 + M$</td>
</tr>
<tr>
<td>$b_{22}$</td>
<td>$NO_3 + OH + M$ $\rightarrow$ $HNO_3 + M$</td>
</tr>
<tr>
<td>$b_{23}$</td>
<td>$NO_2 + HO_2 + M$ $\rightarrow$ $HO_2NO_2 + M$</td>
</tr>
<tr>
<td>$b_{24}$</td>
<td>$HO_2NO_2 + M$ $\rightarrow$ $HO_2 + NO_2 + M$</td>
</tr>
<tr>
<td>$b_{27}$</td>
<td>$HNO_3 + OH$ $\rightarrow$ $H_2O + NO_3$</td>
</tr>
<tr>
<td>$b_{28}$</td>
<td>$HO_2NO_2 + OH$ $\rightarrow$ $H_2O + NO_2 + O_2$</td>
</tr>
<tr>
<td>$b_{32}$</td>
<td>$N_2O_5 + M$ $\rightarrow$ $NO_2 + NO_3 + M$</td>
</tr>
<tr>
<td>$b_{38}^1$</td>
<td>$N_2O + O^{1D}$ $\rightarrow$ $N_2 + O_2$</td>
</tr>
<tr>
<td>$b_{39}^1$</td>
<td>$N_2O + O^{1D}$ $\rightarrow$ $NO + NO$</td>
</tr>
<tr>
<td>Carbon reactions</td>
<td></td>
</tr>
<tr>
<td>$c_2$</td>
<td>$CH_4 + OH$ $\rightarrow$ $CO + 2H_2O + products$</td>
</tr>
</tbody>
</table>

The same superscript number represents different pathways.
Table 2c. Gas Phase Reactions

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_0$</td>
<td>$CH_3Cl + OH \rightarrow Cl + H_2O + products$</td>
</tr>
<tr>
<td>$d_2$</td>
<td>$Cl + O_3 \rightarrow ClO + O_2$</td>
</tr>
<tr>
<td>$d_3$</td>
<td>$ClO + O \rightarrow Cl + O_2$</td>
</tr>
<tr>
<td>$d_4$</td>
<td>$ClO + NO \rightarrow Cl + NO_2$</td>
</tr>
<tr>
<td>$d_5$</td>
<td>$Cl + CH_4 \rightarrow HCl + CO + H_2O + products$</td>
</tr>
<tr>
<td>$d_6$</td>
<td>$Cl + H_2 \rightarrow HCl + H$</td>
</tr>
<tr>
<td>$d_7$</td>
<td>$Cl + HO_2 \rightarrow HCl + O_2$</td>
</tr>
<tr>
<td>$d_8$</td>
<td>$ClO + OH \rightarrow Cl + HO_2$</td>
</tr>
<tr>
<td>$d_{11}$</td>
<td>$HCl + OH \rightarrow Cl + H_2O$</td>
</tr>
<tr>
<td>$d_{31}$</td>
<td>$ClO + NO_2 + M \rightarrow ClONO_2 + M$</td>
</tr>
<tr>
<td>$d_{32}$</td>
<td>$ClONO_2 + O \rightarrow ClO + NO_3$</td>
</tr>
<tr>
<td>$d_{33}$</td>
<td>$ClO + HO_2 \rightarrow HOCl + O_2$</td>
</tr>
<tr>
<td>$d_{34}$</td>
<td>$HOCl + OH \rightarrow H_2O + ClO$</td>
</tr>
<tr>
<td>$d_{35}$</td>
<td>$HOCl + O \rightarrow OH + ClO$</td>
</tr>
<tr>
<td>$d_{36}$</td>
<td>$Cl + NO_2 + M \rightarrow ClNO_2 + M$</td>
</tr>
<tr>
<td>$d_{37}$</td>
<td>$HOCl + Cl \rightarrow OH + Cl_2$</td>
</tr>
<tr>
<td>$d_{60}$</td>
<td>$ClO + ClO + M \rightarrow Cl_2O_2 + M$</td>
</tr>
<tr>
<td>$d_{61}$</td>
<td>$Cl_2O_2 + M \rightarrow ClO + ClO + M$</td>
</tr>
<tr>
<td>$d_{62}$</td>
<td>$OCIO + OH \rightarrow HOCl + O_2$</td>
</tr>
<tr>
<td>$d_{63}$</td>
<td>$OCIO + Cl \rightarrow ClO + ClO$</td>
</tr>
<tr>
<td>$d_{64}$</td>
<td>$OCIO + O \rightarrow ClO + O_2$</td>
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<tr>
<td>$d_{65}$</td>
<td>$OCIO + NO \rightarrow ClO + NO_2$</td>
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<td>$d_{101}$</td>
<td>$CCl_4 + O^{1D} \rightarrow 4Cl + products$</td>
</tr>
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<td>$d_{102}$</td>
<td>$CFCl_3 + O^{1D} \rightarrow 3Cl + HF + products$</td>
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<tr>
<td>$d_{103}$</td>
<td>$CF_2Cl_2 + O^{1D} \rightarrow 2Cl + COF_2 + products$</td>
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<tr>
<td>$e_2$</td>
<td>$Br + O_3 \rightarrow BrO + O_2$</td>
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<td>$BrO + O \rightarrow Br + O_2$</td>
</tr>
<tr>
<td>$e_4$</td>
<td>$BrO + NO \rightarrow NO_2 + Br$</td>
</tr>
<tr>
<td>$e_{5a}$</td>
<td>$BrO + ClO \rightarrow OClO + Br$</td>
</tr>
<tr>
<td>$e_{5b}$</td>
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<td>$e_{5c}$</td>
<td>$BrO + ClO \rightarrow BrCl + O_2$</td>
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<tr>
<td>$e_6$</td>
<td>$BrO + BrO \rightarrow 2Br + O_2$</td>
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<tr>
<td>$e_7$</td>
<td>$Br + HO_2 \rightarrow HBr + O_2$</td>
</tr>
<tr>
<td>$e_8$</td>
<td>$Br + OClO \rightarrow BrO + ClO$</td>
</tr>
<tr>
<td>$e_{11}$</td>
<td>$HBr + OH \rightarrow H_2O + Br$</td>
</tr>
<tr>
<td>$e_{13}$</td>
<td>$BrO + NO_2 + M \rightarrow BrONO_2 + M$</td>
</tr>
<tr>
<td>$e_{15}$</td>
<td>$BrO + HO_2 \rightarrow HOBr + O_2$</td>
</tr>
<tr>
<td>$e_{91}$</td>
<td>$CF_3Br + O^{1D} \rightarrow Br + COF_2 + HF + \text{products}$</td>
</tr>
<tr>
<td>$e_{92}$</td>
<td>$CF_2ClBr + O^{1D} \rightarrow Br + Cl + COF_2 + \text{products}$</td>
</tr>
<tr>
<td>$e_{93}$</td>
<td>$CH_3Br + O^{1D} \rightarrow Br + \text{products}$</td>
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### Table 3. Photochemical Reactions

<table>
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<th>No.</th>
<th>Reactions</th>
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<tr>
<td>01</td>
<td>$O_2 + h\nu$ $\rightarrow O + O$</td>
</tr>
<tr>
<td>02₁</td>
<td>$O_3 + h\nu$ $\rightarrow O + O_2$</td>
</tr>
<tr>
<td>03</td>
<td>$H_2O + h\nu$ $\rightarrow H + OH$</td>
</tr>
<tr>
<td>04₁</td>
<td>$N_2O + h\nu$ $\rightarrow N_2 + O^{1D}$</td>
</tr>
<tr>
<td>05</td>
<td>$CH_4 + h\nu$ $\rightarrow CO + H_2O + H + products$</td>
</tr>
<tr>
<td>06*</td>
<td>$NO_2 + h\nu$ $\rightarrow NO + O$</td>
</tr>
<tr>
<td>07*</td>
<td>$HNO_3 + h\nu$ $\rightarrow NO_2 + OH$</td>
</tr>
<tr>
<td>08</td>
<td>$HOCI + h\nu$ $\rightarrow CI + OH$</td>
</tr>
<tr>
<td>09</td>
<td>$HO_2NO_2 + h\nu$ $\rightarrow HO_2 + NO_2$</td>
</tr>
<tr>
<td>10₂</td>
<td>$ClONO_2 + h\nu$ $\rightarrow Cl + NO_3$</td>
</tr>
<tr>
<td>11*</td>
<td>$N_2O_5 + h\nu$ $\rightarrow NO_3 + NO_2$</td>
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<tr>
<td>12₁</td>
<td>$O_3 + h\nu$ $\rightarrow O^{1D} + O_2$</td>
</tr>
<tr>
<td>13*</td>
<td>$H_2O_2 + h\nu$ $\rightarrow OH + OH$</td>
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<tr>
<td>14</td>
<td>$OCIO + h\nu$ $\rightarrow O + ClO$</td>
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<td>15</td>
<td>$Cl_2O_2 + h\nu$ $\rightarrow Cl + Cl + O_2$</td>
</tr>
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<td>16</td>
<td>$HCl + h\nu$ $\rightarrow H + Cl$</td>
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<tr>
<td>17</td>
<td>$Cl_2 + h\nu$ $\rightarrow Cl + Cl$</td>
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<td>18</td>
<td>$CO_2 + h\nu$ $\rightarrow CO + O$</td>
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<tr>
<td>19</td>
<td>$ClNO_2 + h\nu$ $\rightarrow Cl + NO_2$</td>
</tr>
<tr>
<td>20₃</td>
<td>$BrONO_2 + h\nu$ $\rightarrow Br + NO_3$</td>
</tr>
<tr>
<td>21</td>
<td>$BrCl + h\nu$ $\rightarrow Br + Cl$</td>
</tr>
<tr>
<td>22</td>
<td>$HOBr + h\nu$ $\rightarrow Br + OH$</td>
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<tr>
<td>23</td>
<td>$NO + h\nu$ $\rightarrow N + O$</td>
</tr>
<tr>
<td>24₄</td>
<td>$NO_3 + h\nu$ $\rightarrow NO_2 + O$</td>
</tr>
<tr>
<td>25₄</td>
<td>$NO_3 + h\nu$ $\rightarrow NO + O_2$</td>
</tr>
<tr>
<td>26*</td>
<td>$CCl_4 + h\nu$ $\rightarrow 4Cl + products$</td>
</tr>
<tr>
<td>27*</td>
<td>$CFCl_3 + h\nu$ $\rightarrow 3Cl + HF + products$</td>
</tr>
<tr>
<td>28*</td>
<td>$CF_2Cl_2 + h\nu$ $\rightarrow 2Cl + COF_2 + products$</td>
</tr>
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<td>29*</td>
<td>$CH_3Cl + h\nu$ $\rightarrow Cl + products$</td>
</tr>
<tr>
<td>30*</td>
<td>$CH_3Br + h\nu$ $\rightarrow Br + products$</td>
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<tr>
<td>31*</td>
<td>$CF_2ClBr + h\nu$ $\rightarrow Br + Cl + COF_2 + products$</td>
</tr>
<tr>
<td>32*</td>
<td>$CF_3Br + h\nu$ $\rightarrow Br + COF_2 + HF + products$</td>
</tr>
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<td>33₂</td>
<td>$ClONO_2 + h\nu$ $\rightarrow ClO + NO_2$</td>
</tr>
<tr>
<td>3₄₃</td>
<td>$BrONO_2 + h\nu$ $\rightarrow BrO + NO_2$</td>
</tr>
<tr>
<td>3₅</td>
<td>$COF_2 + h\nu$ $\rightarrow 2HF + products$</td>
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</table>

*: temperature dependency is taken into account. The same subscript number represents different pathways.
Fig. 1. Vertical spacing configuration for the 45-level (green) and 68-level (black) models.

Fig. 2. Root-mean-square wind ($m$ sec$^{-1}$) at the lowest level for Hines gravity wave drag (GWD) scheme.
Fig. 3. Photolysis coefficient (sec\(^{-1}\)) profiles of 35 species determined under clear sky with surface albedo = 0.3 at a solar zenith angle 30° for a standard ozone profile.
Fig. 4a. Exponent of photolysis coefficient (sec\(^{-1}\)) as a function of the solar zenith angle and altitude under clear sky with a surface albedo 0.3 for a standard ozone profile: \(O_2 + h\gamma\rightarrow O + O, O_3 + h\gamma\rightarrow O + O_2, H_2O + h\gamma\rightarrow H + OH,\) and \(N_2O + h\gamma\rightarrow N_2 + O^1D.\)

Fig. 4b. Same as in Fig. 4a except for \(CH_4 + h\gamma\rightarrow CO + H_2O + H^\bullet + \text{products}, NO_2 + h\gamma\rightarrow NO + O, HNO_3 + h\gamma\rightarrow NO_2 + OH,\) and \(HOCl + h\gamma\rightarrow Cl + OH.\)
Fig. 4c. Same as in Fig. 4a except for \( \text{HO}_2\text{NO}_2 + \text{hv} \rightarrow \text{HO}_2 + \text{NO}_2, \text{ClONO}_2 + \text{hv} \rightarrow \text{Cl} + \text{NO}_3, \text{N}_2\text{O}_3 + \text{hv} \rightarrow \text{NO}_3 + \text{NO}_2, \text{and O}_3 + \text{hv} \rightarrow \text{O}_3^+ + \text{O}_2. \)

Fig. 4d. Same as in Fig. 4a except for \( \text{H}_2\text{O}_2 + \text{hv} \rightarrow \text{OH} + \text{OH}, \text{OCIO} + \text{hv} \rightarrow \text{O} + \text{ClO}, \text{Cl}_2\text{O}_2 + \text{hv} \rightarrow \text{Cl} + \text{Cl} + \text{O}_2, \text{and HCl} + \text{hv} \rightarrow \text{H} + \text{Cl}. \)
Fig. 4e. Same as in Fig. 4a except for $Cl_2 + hv \rightarrow Cl + Cl$, $CO_2 + hv \rightarrow CO + O$, $CINO_2 + hv \rightarrow Cl + NO_2$, and $BrONO_2 + hv \rightarrow Br + NO_3$.

Fig. 4f. Same as in Fig. 4a except for $BrCl + hv \rightarrow Br + Cl$, $HOBr + hv \rightarrow Br + OH$, $NO + hv \rightarrow N + O$, and $NO_3 + hv \rightarrow NO_2 + O$. 
Fig. 4g. Same as in Fig. 4a except for NO$_3$ + hv → NO + O$_2$, CCl$_4$ + hv → 4Cl + products, CFCl$_3$ + hv → 3Cl + HF + products, and CF$_2$Cl$_2$ + hv → 2Cl + COF$_2$ + products.

Fig. 4h. Same as in Fig. 4a except for CH$_3$Cl + hv → Cl + products, CH$_3$Br + hv → Br + products, CF$_2$ClBr + hv → Br + Cl + COF$_2$ + products, and CF$_3$Br + hv → Br + COF$_2$ + HF + products.
Fig. 4i. Same as in Fig. 4a except for $\text{ClONO}_2 + hv \rightarrow \text{ClO} + \text{NO}_2$, $\text{BrONO}_2 + hv \rightarrow \text{BrO} + \text{NO}_2$, and $\text{COF}_2 + hv \rightarrow 2\text{HF} + \text{products}$. 
Fig. 5. Solar zenith angles taking into account (red curve) and not taking into account (green line) sphericity for solar zenith angles greater than 65°. Calculation for the inclusion of sphericity is based on the simplified Chapman function, which is nearly independent of height for the vertical range of the current model top at 0.01 hPa.

Fig. 6. Relative difference (%) in the photolysis coefficient for \( \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}, \text{O}_2 + h\nu \rightarrow \text{O} + \text{O}, \) and \( \text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H} \) between the solar maximum and the solar minimum.
Fig. 7. Evolution (1980-2004) of stratospheric aerosols as function of latitude: (upper) optical depth at 550 nm; (lower) effective radius in $\mu$m (extended data of Sato et al., 1993).
Fig. 8. Latitude-pressure cross section of the observed (ERA-40) zonal-mean zonal wind ($m \text{ sec}^{-1}$) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999).

Fig. 9a. Latitude-pressure cross section of the simulated zonal-mean zonal wind ($m \text{ sec}^{-1}$) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM52 simulation.
Fig. 9b. Latitude-pressure cross section of the simulated zonal-mean zonal wind (m sec$^{-1}$) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM53 simulation.

Fig. 9c. Latitude-pressure cross section of the simulated zonal-mean zonal wind (m sec$^{-1}$) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM54 simulation.
Fig. 9d. Latitude-pressure cross section of the simulated zonal-mean zonal wind ($\text{m sec}^{-1}$) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM55 simulation.

Fig. 9e. Latitude-pressure cross section of the simulated zonal-mean zonal wind ($\text{m sec}^{-1}$) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM56 simulation.
Fig. 9f. Latitude-pressure cross section of the simulated zonal-mean zonal wind (m sec$^{-1}$) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). Ensemble mean (PRM52-56).
Fig. 10. Latitude-pressure cross section of the observed (ERA-40) zonal-mean temperature (K) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999).

Fig. 11a. Latitude-pressure cross section of the simulated zonal-mean temperature (K) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM52 simulation.
Fig. 11b. Latitude-pressure cross section of the simulated zonal-mean temperature (K) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999), PRM53 simulation.

Fig. 11c. Latitude-pressure cross section of the simulated zonal-mean temperature (K) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999), PRM54 simulation.
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Fig. 11d. Latitude-pressure cross section of the simulated zonal-mean temperature (K) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM55 simulation.

Fig. 11e. Latitude-pressure cross section of the simulated zonal-mean temperature (K) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM56 simulation.
Fig. 11f. Latitude-pressure cross section of the simulated zonal-mean temperature (K) (contours) and its interannual variations (shading) during four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). Ensemble mean (PRM52-56).
Fig. 12. Latitude-pressure cross section of the observed (SBUV) zonal-mean ozone (ppmv) (contours) and its interannual variations (shading) for four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999).

Fig. 13a. Latitude-pressure cross section of the simulated zonal-mean ozone (ppmv) (contours) and its interannual variations (shading) for four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM52 simulation.
Fig. 13b. Latitude-pressure cross section of the simulated zonal-mean ozone (ppmv) (contours) and its interannual variations (shading) for four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM53 simulation.

Fig. 13c. Latitude-pressure cross section of the simulated zonal-mean ozone (ppmv) (contours) and its interannual variations (shading) for four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM54 simulation.
Fig. 13d. Latitude-pressure cross section of the simulated zonal-mean ozone (ppmv) (contours) and its interannual variations (shading) for four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM55 simulation.

Fig. 13e. Latitude-pressure cross section of the simulated zonal-mean ozone (ppmv) (contours) and its interannual variations (shading) for four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). PRM56 simulation.
Fig. 13f. Latitude-pressure cross section of the simulated zonal-mean ozone (ppmv) (contours) and its interannual variations (shading) for four seasons (December-February, March-May, June-August, and September-November) over 10 years (1990-1999). Ensemble mean (PRMS2-56).
Fig. 14a. Month-latitude cross sections of the 10-year average of the simulated zonal-mean total ozone (DU) for the five members during the 1990s.

Fig. 14b. Month-latitude cross sections of the 10-year average of the simulated zonal-mean total ozone (DU) for the ensemble mean of the five members (left) and the observation data (TOMS/SBUV) (right).
Fig. 15a. Evolutions of the zonal-mean total ozone (DU) latitudinal distribution for the five members from 1980 to 2004.
Fig. 15b. Evolutions of the zonal-mean total ozone (DU) latitudinal distribution for the ensemble mean of the five members (upper) and the observation data (TOMS/SBUV) (lower). Dotted lines indicate the eruption dates of El Chichón and Mount Pinatubo.
Fig. 16. Evolutions of the maximum ozone hole area (< 220 DU) (10^6 km^2, upper) and minimum total ozone (DU, lower) for the observation data (TOMS/SBUV) (blue circles) and simulations of the five members (red squares).
Fig. 17. Evolutions of the deseasonalized zonal-mean zonal wind (m sec$^{-1}$, ERA-40), temperature (K, ERA-40), averaged between 5\textdegree S and 5\textdegree N, and total ozone (ppmv, HALOE) averaged between 10\textdegree S and 10\textdegree N.
Fig. 18. Evolutions of the simulated deseasonalized zonal-mean zonal wind (m sec$^{-1}$) averaged between 5$^\circ$S and 5$^\circ$N for the five members.
Fig. 19. Evolutions of the simulated deseasonalized zonal-mean temperature (K) averaged between 5°S and 5°N for the five members.
Fig. 20. Evolutions of the simulated deseasonalized zonal-mean ozone (ppmv) averaged between 5°S and 5°N for the five members.
Fig. 21a. Power spectrum of the zonal-mean zonal wind averaged between 10°S and 10°N in period-altitude space for the five members of the simulations.
Fig. 21b. Power spectrum of the zonal-mean zonal wind averaged between 10°S and 10°N in period-altitude space for the ensemble mean of the five members (left) and observation data (ERA-40) (right).
Fig. 22a. Latitude-pressure cross sections of the zonal-mean temperature linear trend (K/decade) from 200 to 0.1 hPa. The shading denotes the area of the linear trend different from zero at the 95 % confidence level (t-test) for the five members of the simulation (contour interval is 0.25 K/decade).
Fig. 22b. Latitude-pressure cross sections of the zonal-mean temperature linear trend (K/decade) from 200 to 0.1 hPa. The shading denotes the area of the linear trend different from zero at the 95% confidence level (t-test) for the ensemble mean of the five members (left, contour interval is 0.25 K/decade) and the observation data (ERA-40) (right, contour interval 0.5 K/decade).
Fig. 23a. Latitude-pressure cross sections of the ozone linear trend (%/decade) from 200 to 0.1 hPa. The shading denotes the area of the linear trend different from zero at the 95% confidence level (t-test). The contour interval is 2%/decade for the five members of the simulation.
Fig. 23b. Latitude-pressure cross sections of the ozone linear trend (%/decade) from 200 to 0.1 hPa. The shading denotes the area of the linear trend different from zero at the 95% confidence level (t-test). The contour interval is 2%/decade for the ensemble mean of the five members (left), and observation data sets (SBUV, upper right, SAGE I/II, lower right).
Fig. 24a. Month-latitude cross sections of the total ozone trend (DU/decade). The contour interval is 0.5, DU/decade, and shading denotes the 95% confidence level (t-test) for the five members of the simulation.
Fig. 24b. Month-latitude cross sections of the total ozone trend (DU/decade). The contour interval is 0.5, DU/decade, and shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left) and the observation data (TOMS/SBUV, right).
Fig. 25a. Month-latitude cross sections of the QBO20 total ozone signal in DU per 10m sec\(^{-1}\). The contour interval is 1m sec\(^{-1}\), and shading denotes the 95% confidence level (t-test) for the five members of the simulation.
Fig. 25b. Month-latitude cross sections of the QBO20 total ozone signal in DU per 10 m sec$^{-1}$. The contour interval is 1 m sec$^{-1}$, and shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left) and the observation data (TOMS/SBUV, right).
Fig. 26a. Month-latitude cross sections of the QBO50 total ozone signal in DU per 10 m sec\(^{-1}\). The contour interval is 1 m sec\(^{-1}\), and shading denotes the 95% confidence level (t-test) for the five members of the simulation.
Fig. 26b. Month-latitude cross sections of the QBO50 total ozone signal in DU per 10m sec\(^{-1}\). The contour interval is 1m sec\(^{-1}\), and shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left) and TOMS/SBUV data set (right).
Fig. 27a. Latitude-pressure cross sections of the QBO20 zonal wind signal (\(m\,sec^{-1}/(10\,m\,sec^{-1})\)) between 60°S and 60°N. Contour interval is 2 (\(m\,sec^{-1}/(10\,m\,sec^{-1})\) and shading denotes the 95% confidence level (t-test) for the five members the simulation.
Fig. 27b. Latitude-pressure cross sections of the QBO20 zonal wind signal \((\text{m sec}^{-1})/(10\text{m sec}^{-1})\) between 60°S and 60°N. Contour interval is 2 \((\text{m sec}^{-1})/(10\text{m sec}^{-1})\) and shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left) and the observation data (ERA-40, right).
Fig. 28a. Latitude-pressure cross sections of the QBO50 zonal wind signal \( ((m\text{ sec}^{-1})/(10m\text{ sec}^{-1})) \) between 60°S and 60°N. Contour interval is 2 \( (m\text{ sec}^{-1})/(10m\text{ sec}^{-1}) \) and shading denotes the 95% confidence level (t-test) for the five members the simulation.
Fig. 28b. Latitude-pressure cross sections of the QBO50 zonal wind signal \( (m \text{ sec}^{-1})/(10 \text{ m sec}^{-1}) \) between 60°S and 60°N. Contour interval is 2 \( (m \text{ sec}^{-1})/(10 \text{ m sec}^{-1}) \) and shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left) and the observation data (ERA-40, right).
Fig. 29a. Latitude-pressure cross sections of the QBO20 temperature signal ($K/(10m\,sec^{-1})$) between 60°S and 60°N. Contour interval is 0.2 ($K/(10m\,sec^{-1})$) and shading denotes the 95% confidence level (t-test) for the five members the simulation.
Fig. 29b. Latitude-pressure cross sections of the QBO20 temperature signal ($K/(10m/s^2)$) between 60°S and 60°N. Contour interval is 0.2 ($K/(10m/s^2)$) and shading denotes the 95 % confidence level (t-test) for the ensemble mean of the five members (left) and the observation data (ERA-40, right).
Fig. 30a. Latitude-pressure cross sections of the QBO50 temperature signal (\(K/(10 \text{ m sec}^{-1})\)) between 60°S and 60°N. Contour interval is 0.2 (\(K/(10 \text{ m sec}^{-1})\)) and shading denotes the 95% confidence level (t-test) for the five members the simulation.
Fig. 30b. Latitude-pressure cross sections of the QBO50 temperature signal ($K/(10^3 \text{m sec}^{-1})$) between 60°S and 60°N. Contour interval is 0.2 ($K/(10^3 \text{m sec}^{-1})$) and shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left) and the observation data (ERA-40, right).
Fig. 31a. Latitude-pressure cross sections of the QBO20 ozone (%/(10 m sec⁻¹)) between 60°S and 60°N. Contour interval is 0.4 (%/(10 m sec⁻¹)) and shading denotes the 95 % confidence level (t-test) for the five members the simulation.
Fig. 31b. Latitude-pressure cross sections of the QBO20 ozone (%/(10 m sec\(^{-1}\))) between 60°S and 60°N. Contour interval is 0.4 (%/(10 m sec\(^{-1}\))) and shading denotes the 95 % confidence level (t-test) for the ensemble mean of the five members (left) and the observation data (SBUV, right).
Fig. 32a. Latitude-pressure cross sections of the QBO50 ozone (%/(10 m sec$^{-1}$)) between 60°S and 60°N. Contour interval is 0.4 (%/(10 m sec$^{-1}$)) and shading denotes the 95 % confidence level (t-test) for the five members the simulation.
Fig. 32b. Latitude-pressure cross sections of the QBO50 ozone (%/\(\text{10 m sec}^{-1}\)) between 60°S and 60°N. Contour interval is 0.4 (%/\(\text{10 m sec}^{-1}\)) and shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left) and the observation data (SBUV, right).
Fig. 33a. Latitude-pressure cross sections of the solar temperature signals in K per 100 solar units from 100 to 0.1 hPa; shading denotes the 95 % confidence level (t-test) for the five members of the simulation (contour interval is 0.1).
Fig. 33b. Latitude-pressure cross sections of the solar temperature signals in K per 100 solar units from 100 to 0.1 hPa; shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left, contour interval is 0.1) and the observation data (ERA-40) (right, contour interval is 0.2).
Fig. 34a. Latitude-pressure cross sections of the solar ozone signals in % per 100 solar units from 100 to 0.1 hPa. The contour interval is 0.4, and shading denotes the 95% confidence level (t-test) for the five members of the simulation.
Fig. 34b. Latitude-pressure cross sections of the solar ozone signals in % per 100 solar units from 100 to 0.1 hPa. The contour interval is 0.4, and shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left) and the observation data sets (SBUV, upper right; SAGE I/II, lower right).
Fig. 35a. Latitude-pressure cross sections of the annual average ENSO signal of zonal-mean wind in (m sec$^{-1}$) per -1 standard deviation of SOI. The contour interval is 0.4 and shading denotes the 95 % confidence level (t-test) for the five members of the simulation.
Fig. 35b. Latitude-pressure cross sections of the annual average ENSO signal of zonal-mean wind in \((msec^{-1})\) per -1 standard deviation of SOI. The contour interval is 0.4 and shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left) and the observation data (ERA-40) (right).
Fig. 36a. Latitude-pressure cross sections of the annual average ENSO signal of zonal-mean temperature in (K) per -1 standard deviation of SOI. The contour interval is 0.2 and shading denotes the 95% confidence level (t-test) for the five members of the simulation.
Fig. 36b. Latitude-pressure cross sections of the annual average ENSO signal of zonal-mean temperature in (K) per -1 standard deviation of SOI. The contour interval is 0.2 and shading denotes the 95% confidence level (t-test) for the ensemble mean of the five members (left) and the observation data (ERA-40) (right).
Fig. 37a. Latitude-pressure cross sections of the annual average ENSO signal of zonal-mean ozone in (%) per -1 standard deviation of SOI. The contour interval is 0.3 and shading denotes the 95% confidence level (t-test) for the five members of the simulation.
Fig. 37b. Latitude-pressure cross sections of the annual average ENSO signal of zonal-mean ozone in (%) per -1 standard deviation of SOI. The contour interval is 0.3 and shading denotes the 95% confidence level (t-test) b, for the ensemble mean of the five members (left) and the observation data (SBUV) (right).
Fig. 38a. Time-pressure cross sections of the global (65°S to 65°N) temperature after the El Chichón eruption. The contour interval is 0.5 K and dashed contours denote negative values. Zero contours are omitted for the five members of the simulation.
Fig. 38b. Time-pressure cross sections of the global (65°S to 65°N) temperature after the El Chichón eruption. The contour interval is 0.5 K and dashed contours denote negative values. Zero contours are omitted for the ensemble mean of the five members (left) and the observation data (ERA-40) (right).
Fig. 39a. Time-pressure cross sections of the global (65°S to 65°N) temperature after the Pinatubo eruption. The contour interval is 0.5 K and dashed contours denote negative values. Zero contours are omitted for the five members of the simulation.
Fig. 39b. Time-pressure cross sections of the global (65°S to 65°N) temperature after the Pinatubo eruption. The contour interval is 0.5 K and dashed contours denote negative values. Zero contours are omitted for the ensemble mean of the five members (left) and the observation data (ERA-40) (right).
Fig. 40a. Evolution of the global total ozone after the El Chichón eruption for the five members of the simulation.
Fig. 40b. Evolution of the global total ozone after the El Chichón eruption for the ensemble mean of the five members (left) and the observation data (TOMS/SBUV) (right).
Fig. 41a. Evolution of the global total ozone after the Pinatubo eruption for the five members of the simulation.
Fig. 41b. Evolution of the global total ozone after the Pinatubo eruption for the ensemble mean of the five members (left) and the observation data (TOMS/SBUV) (right).
Fig. I-1. Schematic comparison between (a) the ordinary semi-Lagrange transport scheme and (b) the hybrid semi-Lagrange transport scheme.
Fig. I-2. Schematic illustration showing how the mixing ratio in the $\tilde{q}^-$ in $\tilde{p}^-$ ordinate is calculated from $q^-$ in the $p^-$ ordinate. Note that the vertical advection alters the pressure ordinate from $p^-$ to $\tilde{p}^-$, not the mixing ratio profile. Then, $\tilde{q}^-_t$ is defined as the mixing ratio contained in $\Delta \tilde{p}^-_T$. See the text for details.
Fig. 1-3. (Upper) Configuration of the four sequentially aligned cells. From the cell-averages (histograms) of the four cells, the in-cell profile (solid curve) of the i-th cell between $x_{i-1/2}$ and $x_{i+1/2}$ is calculated by using a cubic polynomial. (Lower) Configuration of the integral (shaded area) of the in-cell profile (solid curve) between $p_{i+1/2}$ and $p$. The interface values of the i-th cell are denoted by $f_{i+1/2}$ and $f_{i-1/2}$. 
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